

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of

Date: May 15, 2008

Applicants: Bednorz et al.

Docket: YO987-074BZ

Serial No.: 08/479,810

Group Art Unit: 1751

Filed: June 7, 1995

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Commissioner for Patents  
United States Patent and Trademark Office  
P.O. Box 1450  
Alexandria, VA 22313-1450

**APPEAL BRIEF  
PART IX**

**CFR 37 § 41.37(c) (1) (ix)**

**SECTION 1**

**VOLUME 5**

**Part 1**

**BRIEF ATTACHMENTS AA TO AL**

Respectfully submitted,

/Daniel P Morris/  
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Reg. No. 32,053  
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IBM CORPORATION  
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P.O. Box 218  
Yorktown Heights, New York 10598

# **BRIEF ATTACHMENT AA**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of

Applicants: Bednorz et al.

Serial No.: 08/479,810

Filed: June 7, 1995

For: **NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION**

Date: March 1, 2005

Docket: YO987-074BZ

Group Art Unit: 1751

Examiner: M. Kopec

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

**FIRST SUPPLEMENTAL AMENDMENT**

Sir:

In response to the Office Action dated July 28, 2004, please consider the  
following:

**ATTACHMENT AA**

1989

Powder Diffraction File

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# Inorganic Phases

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Alphabetical Index (Chemical and Mineral Name)



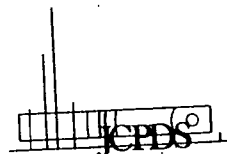
INTERNATIONAL CENTRE FOR DIFFRACTION DATA



# Powder Diffraction File

## Alphabetical Index Inorganic Phases 1989

Compiled by the JCPDS—International Centre for Diffraction Data in cooperation with the American Ceramic Society, American Crystallographic Association, American Society for Testing and Materials, Australian X-Ray Analytical Association, British Crystallographic Association, The Clay Minerals Society, Deutsche Mineralogische Gesellschaft, The Institute of Physics, The Mineralogical Association of Canada, The Mineralogical Society of America, Mineralogical Society of Great Britain and Ireland, National Association of Corrosion Engineers, and Société Française de Minéralogie et de Cristallographie.



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*Joint Committee on Powder Diffraction Standards*

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Printed in U.S.A.  
1989



File No.	File No.	File No.	File No.
Mercury : Magnesium	Hg <sub>2</sub> Hg	3.77x	2.37
Mercury : Magnesium	Hg <sub>2</sub> Hg	3.58x	2.47x
Mercury : Magnesium	e-Hg <sub>2</sub> Hg	3.44x	2.46x
Mercury : Magnesium	Hg <sub>2</sub> Hg	3.39x	3.45x
Mercury : Magnesium	Hg <sub>2</sub> Hg	2.33x	1.48x
Mercury Manganese Fluoride :	HgMnF <sub>6</sub>	3.72x	2.75x
Mercury Manganese Fluoride :	Hg <sub>2</sub> MnF <sub>6</sub>	3.21x	1.94x
Mercury Manganese Fluoride :	Hg <sub>2</sub> MnF <sub>6</sub>	6.34x	4.50x
Mercury Manganese Fluoride :	Hg <sub>2</sub> MnF <sub>6</sub>	3.24x	3.04x
Mercury Manganese Fluoride :	Hg <sub>2</sub> MnF <sub>6</sub>	3.47x	2.31x
Mercury Manganese Fluoride :	Hg <sub>2</sub> MnF <sub>6</sub>	2.97x	6.50x
Mercury Manganese Fluoride :	Hg <sub>2</sub> MnF <sub>6</sub>	3.31x	4.14x
Mercury Manganese Fluoride :	Hg <sub>2</sub> MnF <sub>6</sub>	2.16x	2.11x
Mercury Manganese Fluoride :	Hg <sub>2</sub> MnF <sub>6</sub>	3.01x	1.74x
Mercury Manganese Fluoride :	Hg <sub>2</sub> MnF <sub>6</sub>	3.10x	1.62x
Mercury Manganese Fluoride :	(NH <sub>4</sub> ) <sub>2</sub> Hg(NO <sub>3</sub> ) <sub>6</sub>	2.34x	2.14x
Mercury Manganese Fluoride :	C <sub>6</sub> H <sub>12</sub> N <sub>4</sub> Ni(NO <sub>3</sub> ) <sub>12</sub>	2.26x	1.48x
Mercury Manganese Fluoride :	K <sub>2</sub> Hg(NO <sub>3</sub> ) <sub>6</sub>	2.09x	1.38x
Mercury Manganese Fluoride :	Rb <sub>2</sub> Hg(NO <sub>3</sub> ) <sub>6</sub>	2.14x	1.40x
Mercury Manganese Fluoride :	Tl <sub>2</sub> Hg(NO <sub>3</sub> ) <sub>6</sub>	2.13x	1.39x
Mercury Manganese Fluoride :	Hg <sub>2</sub> Ni <sub>2</sub> F <sub>6</sub>	2.98x	1.83x
Mercury Manganese Fluoride :	Hg <sub>2</sub> Nb <sub>2</sub> F <sub>6</sub>	3.07x	1.85x
Mercury Manganese Fluoride :	Hg(NO <sub>3</sub> ) <sub>2</sub>	2.87x	4.83x
Mercury Manganese Fluoride :	Hg(NO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O	3.47x	3.75x
Mercury Manganese Fluoride :	Hg(NO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O	4.50x	4.63x
Mercury Manganese Fluoride :	Hg(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O	2.90x	2.88x
Mercury Manganese Fluoride :	Hg(OH)(NO <sub>3</sub> )	5.93x	3.86x
Mercury Manganese Fluoride :	Hg <sub>2</sub> (OH)(NO <sub>3</sub> ) <sub>2</sub>	5.21x	4.81x
Mercury Manganese Fluoride :	Hg <sub>2</sub> (OH)(NO <sub>3</sub> ) <sub>2</sub>	3.38x	4.68x
Mercury Manganese Fluoride :	Hg <sub>2</sub> NO <sub>3</sub> ·PO <sub>4</sub> ·H <sub>2</sub> O	3.77x	7.53x
Mercury Manganese Fluoride :	Hg <sub>2</sub> Cl <sub>2</sub> N <sub>2</sub> ·H <sub>2</sub> O	2.93x	2.79x
Mercury Manganese Fluoride :	NiH <sub>2</sub> O <sub>2</sub> ·2H <sub>2</sub> O	2.54x	1.43x
Mercury Manganese Fluoride :	(Hg <sub>2</sub> NO <sub>3</sub> ) <sub>2</sub> ·2H <sub>2</sub> O	2.54x	2.86x
Mercury Manganese Fluoride :	H <sub>2</sub> S <sub>2</sub> ·H <sub>2</sub> g <sub>2</sub> N	2.35x	2.06x
Mercury Manganese Fluoride :	(Hg <sub>2</sub> NNO <sub>3</sub> ) <sub>2</sub>	5.52x	2.76x
Mercury Manganese Fluoride :	Hg <sub>2</sub> N <sub>2</sub> SO <sub>4</sub>	2.87x	2.74x
Mercury Manganese Fluoride :	CH <sub>3</sub> Hg(NO <sub>3</sub> ) <sub>2</sub>	2.24x	1.47x
Mercury Manganese Fluoride :	RbHg(NO <sub>3</sub> ) <sub>2</sub>	2.23x	1.46x
Mercury Manganese Fluoride :	TlHg(NO <sub>3</sub> ) <sub>2</sub>	2.20x	1.44x
Mercury Manganese Fluoride :	C <sub>2</sub> HgO <sub>2</sub>	3.99x	3.42x
Mercury Manganese Fluoride :	HgO <sub>2</sub>	3.36x	2.73x
Mercury Manganese Fluoride :	HgO <sub>2</sub>	3.18x	3.04x
Mercury Manganese Fluoride :	HgO	2.97x	2.84x
Mercury Manganese Fluoride :	HgO	2.92x	2.55x
Mercury Manganese Fluoride :	α-HgO <sub>2</sub>	2.75x	3.35x
Mercury Manganese Fluoride :	Hg <sub>2</sub> O <sub>2</sub> ·Br <sub>2</sub>	4.02x	2.76x
Mercury Manganese Fluoride :	HgCO <sub>3</sub> ·2HgO	2.75x	2.82x
Mercury Manganese Fluoride :	C <sub>2</sub> HgO <sub>2</sub>	3.22x	1.81x
Mercury Manganese Fluoride :	Hg <sub>2</sub> O <sub>2</sub> (OH) <sub>2</sub>	2.76x	5.93x
Mercury Manganese Fluoride :	HgCl <sub>2</sub> ·3HgO	3.95x	2.70x
Mercury Manganese Fluoride :	(HgCl <sub>2</sub> ) <sub>2</sub> OCl	3.79x	2.47x
Mercury Manganese Fluoride :	Hg <sub>2</sub> OCl <sub>2</sub>	3.76x	2.18x
Mercury Manganese Fluoride :	Hg <sub>2</sub> OCl <sub>2</sub>	3.16x	2.87x
Mercury Manganese Fluoride :	Hg <sub>2</sub> OCl <sub>2</sub>	2.86x	3.01x
Mercury Manganese Fluoride :	Hg <sub>2</sub> OCl <sub>2</sub>	2.84x	2.70x
Mercury Manganese Fluoride :	Hg <sub>2</sub> OCl <sub>2</sub>	2.83x	2.74x
Mercury Manganese Fluoride :	Hg <sub>2</sub> OCl <sub>2</sub>	2.51x	2.76x
Mercury Manganese Fluoride :	Hg <sub>2</sub> Cl <sub>2</sub> (OH)	3.27x	1.89x
Mercury Manganese Fluoride :	Hg <sub>2</sub> OCl(OH)	4.13x	3.09x
Mercury Manganese Fluoride :	Hg <sub>2</sub> OCl(NH <sub>2</sub> )	6.63x	3.93x
Mercury Manganese Fluoride :	Hg <sub>2</sub> Co <sub>2</sub> F <sub>6</sub> O	3.01x	1.84x
Mercury Manganese Fluoride :	Hg <sub>2</sub> MnF <sub>6</sub> ·O	2.97x	5.93x
Mercury Manganese Fluoride :	NaHg <sub>2</sub> O <sub>2</sub>	2.88x	2.19x
Mercury Manganese Fluoride :	Hg <sub>2</sub> O <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	5.71x	3.68x
Mercury Manganese Fluoride :	Hg <sub>2</sub> O <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>	5.03x	4.05x
Mercury Manganese Fluoride :	Hg <sub>2</sub> O <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> ·H <sub>2</sub> O	9.60x	4.79x
Mercury Manganese Fluoride :	Hg(NO <sub>3</sub> ) <sub>2</sub> ·2HgO·H <sub>2</sub> O	4.82x	3.21x
Mercury Manganese Fluoride :	Rb <sub>2</sub> HgO <sub>2</sub>	3.10x	1.71x
Mercury Manganese Fluoride :	Hg <sub>2</sub> O <sub>2</sub> ·SeO <sub>4</sub>	3.35x	2.95x
Mercury Manganese Fluoride :	HgSO <sub>4</sub> ·2HgO	2.97x	6.20x
Mercury : Magnesium	Hg <sub>2</sub> SO <sub>4</sub>	2.60x	2.34x
Mercury : Magnesium	Hg <sub>2</sub> SO <sub>4</sub>	2.98x	2.87x
Mercury : Magnesium	Hg <sub>2</sub> SO <sub>4</sub>	10.64x	4.32x
Mercury : Magnesium	Hg <sub>2</sub> SO <sub>4</sub>	2.34x	1.27x
Mercury : Magnesium	Hg <sub>2</sub> SO <sub>4</sub>	2.24x	2.37x
Mercury : Magnesium	Hg <sub>2</sub> SO <sub>4</sub>	2.91x	1.96x
Mercury : Magnesium	Hg <sub>2</sub> SO <sub>4</sub>	3.96x	3.37x
Mercury : Magnesium	Hg <sub>2</sub> SO <sub>4</sub>	3.17x	2.98x
Mercury : Magnesium	Hg <sub>2</sub> SO <sub>4</sub>	2.02x	2.92x
Mercury : Magnesium	Hg <sub>2</sub> SO <sub>4</sub>	2.60x	2.94x
Mercury : Magnesium	Behg(PO <sub>4</sub> ) <sub>3</sub>	5.83x	3.76x
Mercury : Magnesium	Hg <sub>2</sub> P <sub>2</sub> O <sub>7</sub> ·H <sub>2</sub> O	3.22x	3.56x
Mercury : Magnesium	Li <sub>2</sub> Hg(PO <sub>4</sub> ) <sub>2</sub>	6.85x	3.45x
Mercury : Magnesium	AgHg <sub>2</sub> PO <sub>4</sub>	3.15x	2.50x
Mercury : Magnesium	AgHg <sub>2</sub> PO <sub>4</sub>	2.94x	2.68x
Mercury : Magnesium	Hg <sub>2</sub> P <sub>2</sub> S <sub>8</sub>	2.78x	3.32x
Mercury : Magnesium	Hg <sub>2</sub> P <sub>2</sub> S <sub>8</sub>	2.74x	3.23x
Mercury : Magnesium	Hg <sub>2</sub> P <sub>2</sub> S <sub>8</sub>	6.57x	4.38x
Mercury : Magnesium	Hg <sub>2</sub> P <sub>2</sub> S <sub>8</sub>	4.53x	2.96x
Mercury : Magnesium	Hg <sub>2</sub> P <sub>2</sub> S <sub>8</sub>	2.34x	2.09x
Mercury : Magnesium	PHg <sub>2</sub>	2.19x	2.33x
Mercury : Magnesium	PHg <sub>2</sub>	2.19x	2.33x
Mercury : Magnesium	Hg <sub>2</sub> P <sub>2</sub> S <sub>8</sub>	3.81x	1.78x
Mercury : Magnesium	Hg <sub>2</sub> P <sub>2</sub> S <sub>8</sub>	3.11x	2.21x
Mercury : Magnesium	β-Hg <sub>2</sub> Re <sub>2</sub> O <sub>10</sub>	6.44x	3.12x
Mercury : Magnesium	α-Re <sub>2</sub> O <sub>3</sub> ·O <sub>2</sub>	6.37x	3.90x
Mercury : Magnesium	Re <sub>2</sub> Hg <sub>2</sub> O <sub>10</sub>	3.84x	3.51x
Mercury : Magnesium	Re <sub>2</sub> Hg <sub>2</sub> O <sub>10</sub>	3.62x	3.06x
Mercury : Magnesium	Hg <sub>2</sub> P <sub>2</sub> S <sub>8</sub>	3.60x	3.13x
Mercury : Magnesium	Re <sub>2</sub> Hg <sub>2</sub> O <sub>10</sub>	3.58x	7.15x
Mercury : Magnesium	Hg <sub>2</sub> Re <sub>2</sub> O <sub>10</sub> ·Hg <sub>2</sub> O	3.50x	3.59x
Mercury : Magnesium	α-Hg <sub>2</sub> Re <sub>2</sub> O <sub>10</sub> ·2H <sub>2</sub> O	3.71x	4.07x
Mercury : Magnesium	ReHg <sub>2</sub>	2.19x	2.27x
Mercury : Magnesium	Hg <sub>2</sub> Re <sub>2</sub>	3.81x	1.77x
Mercury : Magnesium	HgSc	2.46x	3.48x
Mercury : Magnesium	HgSe	2.38x	1.32x
Mercury : Magnesium	HgSeO <sub>4</sub>	3.35x	3.35x
Mercury : Magnesium	Hg <sub>2</sub> SeO <sub>4</sub> ·H <sub>2</sub> O	5.06x	3.86x
Mercury : Magnesium	Hg <sub>2</sub> Se	3.51x	2.15x
Mercury : Magnesium	HgSe	2.93x	3.52x
Mercury : Magnesium	C <sub>12</sub> H <sub>18</sub> O <sub>2</sub> Se <sub>2</sub>	10.8x	3.66x
Mercury : Magnesium	Hg <sub>2</sub> Br <sub>2</sub> Se <sub>2</sub>	2.68x	2.36x
Mercury : Magnesium	K <sub>2</sub> HgSe <sub>2</sub>	5.92x	2.89x
Mercury : Magnesium	Rb <sub>2</sub> HgSe <sub>2</sub>	2.68x	2.22x
Mercury : Magnesium	Hg <sub>2</sub> (Se <sub>2</sub> )	3.41x	3.28x
Mercury : Magnesium	Hg <sub>2</sub> Tl <sub>2</sub> Se <sub>2</sub>	2.89x	3.27x
Mercury : Magnesium	α-Hg <sub>2</sub> Tl <sub>2</sub> Se <sub>2</sub>	2.92x	2.67x
Mercury : Magnesium	CaHg <sub>2</sub> Se <sub>2</sub> ·H <sub>2</sub> O	3.40x	1.89x
Mercury : Magnesium	Hg <sub>2</sub> SiF <sub>2</sub> ·2H <sub>2</sub> O	5.58x	4.12x
Mercury : Magnesium	Cu <sub>2</sub> Hg <sub>2</sub> Si <sub>2</sub>	3.44x	3.28x
Mercury : Magnesium	Hg <sub>2</sub> Si <sub>2</sub>	3.40x	3.52x
Mercury : Magnesium	Cu <sub>2</sub> Hg <sub>2</sub> Si <sub>2</sub>	3.28x	2.88x
Mercury : Magnesium	γ-Ag <sub>2</sub> Hg <sub>2</sub>	2.36x	1.37x
Mercury : Magnesium	Hg <sub>2</sub> Ag <sub>2</sub>	2.35x	1.36x
Mercury : Magnesium	Ag <sub>2</sub> Hg <sub>2</sub>	2.27x	2.40x
Mercury : Magnesium	(Au <sub>2</sub> Ag) <sub>2</sub> Hg <sub>2</sub>	2.36x	2.22x
Mercury : Magnesium	Hg <sub>2</sub> Na <sub>2</sub>	3.81x	6.03x
Mercury : Magnesium	HgNa	3.75x	3.59x
Mercury : Magnesium	Hg <sub>2</sub> Na	2.60x	2.51x
Mercury : Magnesium	Na <sub>2</sub> Hg <sub>2</sub>	2.60x	2.22x
Mercury : Magnesium	Na <sub>2</sub> Hg <sub>2</sub>	2.55x	2.18x
Mercury : Magnesium	HgSO <sub>4</sub>	3.93x	3.87x
Mercury : Magnesium	Hg <sub>2</sub> SO <sub>4</sub>	3.04x	4.43x
Mercury : Magnesium	2HgSO <sub>4</sub> ·3NH <sub>3</sub>	2.79x	4.09x
Mercury : Magnesium	HgSO <sub>4</sub> ·H <sub>2</sub> O	4.62x	3.60x
Mercury : Magnesium	HgS	3.38x	2.07x
Mercury : Magnesium	Mercury Sulfide /Cinnabar, syn	3.36x	2.86x
Mercury : Magnesium	Mercury Sulfide /Hypercinnabar, syn	3.08x	1.98x
Mercury : Magnesium	C <sub>12</sub> H <sub>18</sub> O <sub>2</sub> Se <sub>2</sub>	10.6x	3.64x

## i Mercury Bromide Oxide Chloride //Comanchemite

## i Mercury Bromide Sulfide :

## i Mercury Bromide Sulfide : Copper

## i Mercury Bromide : Tellurium

## o Mercury Bromide : Tellurium

## i Mercury : Cadmium

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[illegible]

# **BRIEF ATTACHMENT AB**



**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of

Applicants: Bednorz et al.

Serial No.: 08/479,810

Filed: June 7, 1995

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Date: March 14, 2005

Docket: YO987-074BZ

Group Art Unit: 1751

Examiner: M. Kopec

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

**THIRD SUPPLEMENTAL AMENDMENT**

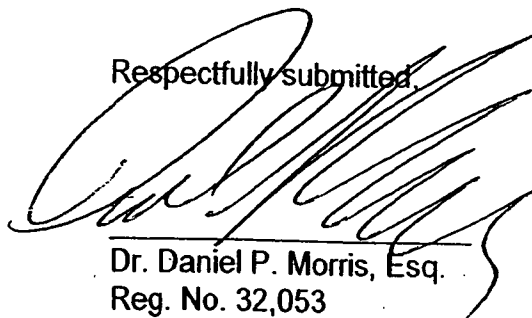
Sir:

In response to the Office Action dated July 28, 2004, please consider the following:

The attachments referred to herein A to Z and AA are in the FIRST SUPPLEMENTAL AMENDMENT. The Attachments AB to AG are attached herein.

Please charge any fee necessary to enter this paper and any previous paper to deposit account 09-0468.

Respectfully submitted,



Dr. Daniel P. Morris, Esq.  
Reg. No. 32,053  
(914) 945-3217

IBM CORPORATION  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, New York 10598

**ATTACHMENT AB**

# Synthesis of cuprate superconductors\*

C N R Rao, R Nagarajan and R Vijayaraghavan

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Received 28 August 1992, in final form 19 October 1992

**Abstract.** There has been unprecedented activity pertaining to the synthesis and characterization of superconducting cuprates in the last few years. A variety of synthetic strategies has been employed to prepare pure monophasic cuprates of different families with good superconducting properties. Besides the traditional ceramic method, other methods such as coprecipitation and precursor methods, the sol-gel method, the alkali flux method and the combustion method have been employed for the synthesis of cuprates. Depending on the requirements, varying conditions such as high oxygen or hydrostatic pressure and low oxygen fugacity are employed in the synthesis. In this review, we discuss the synthesis of the various types of cuprate superconductors and point out the advantages and disadvantages of the different methods. We have provided the necessary preparative details, presenting the crucial information in tabular form wherever necessary.

## 1. Introduction

Since the discovery of high- $T_c$  superconductivity in the La-Ba-Cu-O system [1], a variety of cuprate superconductors with  $T_c$ s going up to 128 K have been synthesized and characterized [2, 3]. No other class of materials has been worked on so widely and intensely in recent years as have the cuprate superconductors. Several methods of synthesis have been employed for preparing the cuprates, with the objective of obtaining pure monophasic products with good superconducting characteristics [3, 4]. The most common method of synthesis of cuprate superconductors is the traditional ceramic method which has been employed for the preparation of a large variety of oxide materials [5]. Although the ceramic method has yielded many of the cuprates with satisfactory characteristics, different synthetic strategies have become necessary in order to control factors such as the cation composition, oxygen stoichiometry, cation oxidation states and carrier concentration. Especially noteworthy amongst these methods are chemical or solution routes which permit better mixing of the constituent cations in order to reduce the diffusion distances in the solid state [3, 6]. Such methods include coprecipitation, use of precursors, the sol-gel method and the use of alkali fluxes. The combustion method or self-propagating high-temperature synthesis (SPS) has also been employed. In this review, we will discuss the preparation of cuprate superconductors by the different methods, mentioning

the special features of each method and the conditions employed for the synthesis. In table 1, we give a list of the cuprate superconductors discussed in this review along with their structural parameters and approximate  $T_c$  values. Preparative conditions such as reaction temperature, oxygen pressure, hydrostatic pressure and annealing conditions are specified in the discussion and given in tabular form where necessary. It is hoped that this review will be found useful by practitioners of the subject as well as those freshly embarking on the synthesis of these materials.

## 2. Ceramic method

The most common method of synthesizing inorganic solids is by the reaction of the component materials at elevated temperatures. If all the components are solids, the method is called the ceramic method [5]. If one of the constituents is volatile or sensitive to the atmosphere, the reaction is carried out in sealed evacuated capsules. Platinum, silica or alumina containers are generally used for the synthesis of metal oxides. The starting materials are metal oxides, carbonates, or other salts, which are mixed, homogenized and heated at a given temperature sufficiently long for the reaction to be completed. A knowledge of the phase diagram is useful in fixing the composition and conditions in such a synthesis.

The ceramic method generally requires relatively high temperatures (up to 2300 K) which are generally attained by resistance heating. Electric arc and skull

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Table 1. Structural parameters and approximate  $T_c$  values of cuprate superconductors.

Cuprate	Structure	$T_c$ (K) (max. value)
1 $\text{La}_2\text{CuO}_{4-x}$	Bmab; $a = 5.355$ , $b = 5.401$ , $c = 13.15$ Å	39
2 $\text{La}_{2-x}\text{Sr}_x(\text{Ba})\text{CuO}_4$	I4/mmm; $a = 3.779$ , $c = 13.23$ Å	35
3 $\text{La}_2\text{Ca}_{1-x}\text{Sr}_x\text{Cu}_2\text{O}_8$	I4/mmm; $a = 3.825$ , $c = 19.42$ Å	60
4 $\text{YBa}_2\text{Cu}_3\text{O}_7$	Pmmm; $a = 3.821$ , $b = 3.885$ , $c = 11.676$ Å	93
5 $\text{YBa}_2\text{Cu}_4\text{O}_8$	Ammm; $a = 3.84$ , $b = 3.87$ , $c = 27.24$ Å	80
6 $\text{Y}_2\text{Ba}_4\text{Cu}_5\text{O}_{13}$	Ammm; $a = 3.851$ , $b = 3.869$ , $c = 50.29$ Å	93
7 $\text{Bi}_2\text{Sr}_2\text{CuO}_8$	Amaa; $a = 5.362$ , $b = 5.374$ , $c = 24.622$ Å	10
8 $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$	A2aa; $a = 5.409$ , $b = 5.420$ , $c = 30.83$ Å	92
9 $\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_2\text{O}_{10}$	A2aa; $a \sim 5.39$ , $b \sim 5.40$ , $c \sim 37$ Å	110
10 $\text{Bi}_2\text{Sr}_2(\text{Ln}_{1-x}\text{Ce}_x)_2\text{Cu}_2\text{O}_{10}$	P4/mmm; $a = 3.888$ , $c = 17.26$ Å	25
11 $\text{Ti}_2\text{Ba}_2\text{CuO}_6$	A2aa; $a = 5.468$ , $b = 5.472$ , $c = 23.238$ Å; I4/mmm; $a = 3.868$ , $c = 23.239$ Å	92
12 $\text{Ti}_2\text{CaBa}_2\text{Cu}_2\text{O}_8$	I4/mmm; $a = 3.855$ , $c = 29.318$ Å	119
13 $\text{Ti}_2\text{Ca}_2\text{Ba}_2\text{Cu}_2\text{O}_{10}$	I4/mmm; $a = 3.85$ , $c = 35.9$ Å	128
14 $\text{Ti}(\text{BaLa})\text{CuO}_6$	P4/mmm; $a = 3.83$ , $c = 9.55$ Å	40
15 $\text{Ti}(\text{SrLa})\text{CuO}_6$	P4/mmm; $a \sim 3.7$ , $c \sim 9$ Å	40
16 $(\text{Ti}_{0.5}\text{Pb}_{0.5})\text{Sr}_2\text{CuO}_5$	P4/mmm; $a = 3.738$ , $c = 9.01$ Å	40
17 $\text{TiCaBa}_2\text{Cu}_2\text{O}_7$	P4/mmm; $a = 3.856$ , $c = 12.754$ Å	103
18 $(\text{Ti}_{0.5}\text{Pb}_{0.5})\text{CaSr}_2\text{Cu}_2\text{O}_7$	P4/mmm; $a = 3.80$ , $c = 12.65$ Å	90
19 $\text{TiSr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_2\text{O}_7$	P4/mmm; $a = 3.80$ , $c = 12.10$ Å	90
20 $\text{TiCa}_2\text{Ba}_2\text{Cu}_2\text{O}_8$	P4/mmm; $a = 3.853$ , $c' = 15.913$ Å	110
21 $(\text{Ti}_{0.5}\text{Pb}_{0.5})\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_8$	P4/mmm; $a = 3.81$ , $c = 15.23$ Å	120
22 $\text{TiBa}_2(\text{Ln}_{1-x}\text{Ce}_x)_2\text{Cu}_2\text{O}_8$	I4/mmm; $a \sim 3.8$ , $c \sim 29.5$ Å	40
23 $\text{Pb}_2\text{Sr}_2\text{Ln}_{0.5}\text{Ca}_{0.5}\text{Cu}_2\text{O}_8$	Cmmm; $a = 5.435$ , $b = 5.463$ , $c = 15.817$ Å	70
24 $\text{Pb}_2(\text{Sr}, \text{La})_2\text{Cu}_2\text{O}_8$	P2 <sub>2</sub> , 2; $a = 5.333$ , $b = 5.421$ , $c = 12.609$ Å	32
25 $(\text{Pb}, \text{Cu})\text{Sr}_2(\text{Ln}, \text{Ca})\text{Cu}_2\text{O}_7$	P4/mmm; $a = 3.820$ , $c = 11.826$ Å	50
26 $(\text{Pb}, \text{Cu})(\text{Sr}, \text{Eu})(\text{Eu}, \text{Ce})\text{Cu}_2\text{O}_7$	I4/mmm; $a = 3.837$ , $c = 29.01$ Å	25
27 $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$	I4/mmm; $a = 3.95$ , $c = 12.07$ Å	30
28 $\text{Ce}_{1-x}\text{Sr}_x\text{CuO}_2$	P4/mmm; $a = 3.902$ , $c = 3.35$ Å	110
29 $\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$	P4/mmm; $a = 3.942$ , $c = 3.393$ Å	40

techniques give temperatures up to 3300 K while high-power  $\text{CO}_2$  lasers give temperatures up to 4300 K. The main disadvantages of the ceramic method are the following:

(i) The starting mixtures are inhomogeneous at the atomic level.

(ii) When no melt is formed during the reaction, the entire reaction has to occur in the solid state, first by a phase boundary reaction at the points of contact between the components and later by the diffusion of the constituents through the product phase. With the progress of the reaction, diffusion paths become longer and the reaction rate slower; the reaction can be speeded up to some extent by intermittent grinding between heating cycles.

(iii) There is no simple way of monitoring the progress of the reaction. It is by trial and error that one decides on the appropriate conditions required for the completion of the reaction. Because of this difficulty, with the ceramic method one often ends up with mixtures of reactants and products. Separation of the desired products from such mixtures is difficult, if not impossible.

(iv) Frequently it becomes difficult to obtain a compositionally homogeneous product even where the reaction proceeds nearly to completion.

Despite the above limitations, the ceramic method is widely used for the synthesis of a large variety of inorganic solids. In the case of the cuprate superconductors,

the ceramic method involves mixing and grinding the component oxides, carbonates or other salts, and heating the mixture, generally in pellet form, at the desired temperature. A common variation of the method is to heat a mixture of nitrates obtained by digesting the metal oxides/carbonates in concentrated  $\text{HNO}_3$  and evaporating the solution to dryness. Heating is carried out in air or in an appropriate atmosphere, controlling the partial pressure of oxygen when necessary. In the case of thallium cuprates, because of the volatility and poisonous nature of the thallium oxide vapour, reactions are carried out in sealed tubes. In some of the earlier preparations, the thallium cuprates were synthesized in open furnaces. This is however, not recommended. A successful synthesis by the ceramic method depends on several factors which include the nature of the starting materials (the choice of oxides, carbonates), the homogeneity of the mixture of powders, the rate of heating as well as the reaction temperature and duration.

## 2.1. $\text{La}_2\text{CuO}_4$ -related 214 cuprates

Synthesis of alkaline-earth-doped  $\text{La}_{1-x}\text{M}_x\text{CuO}_4$  ( $\text{M} = \text{Ca}, \text{Sr}$  and  $\text{Ba}$ ) of  $\text{K}_2\text{NiF}_4$  structure with superconducting transition temperatures up to 35 K is readily achieved by the ceramic method. Typically, the synthesis is carried out by reacting stoichiometric quantities of the oxides and/or carbonates around 1300 K in

oxygen atmosphere at 0.1 K after the sintering step [16]. Metal nitrates have also been used as starting materials for the synthesis [11–13]. By starting with metal nitrates, one obtains a more homogeneous starting mixture, since the hydrated metal nitrates have low melting points leading to a uniform melt in the initial stage of the reaction. Furthermore, nitrates provide an oxidative atmosphere, which is required to obtain the necessary oxygen content.

Stoichiometric  $\text{La}_2\text{CuO}_4$  is an antiferromagnetic insulator.  $\text{La}_2\text{CuO}_4$  prepared under high oxygen pressures, however, shows superconductivity ( $T_c \sim 35$  K) since the oxygen excess introduces holes just as the alkaline earth dopants [14–16].  $\text{La}_2\text{CuO}_{4+\delta}$  ( $\delta$  up to 0.05) has been synthesized by annealing  $\text{La}_2\text{CuO}_4$  under an oxygen pressure of 3 kbar at 870 K [14, 15] or 23 kbar at 1070 K [16]. Oxygen plasma has also been used to increase the oxygen content.

The next homologue of  $\text{La}_2\text{CuO}_4$  containing two Cu–O layers,  $\text{La}_{1-x}\text{Sr}_x\text{CaCu}_2\text{O}_6$  ( $T_c \sim 60$  K), has been synthesized by using high oxygen pressures [17]. The synthesis involves heating the sample at an oxygen pressure of around 20 bar at 1240 K. The material prepared at ambient oxygen pressures (in air) is an insulator. Several other high-oxygen-pressure preparations have been reported on the  $n=2$  member of the  $\text{La}_{2-x}\text{Cu}_2\text{O}_{2+x}$  homologous series by making use of commercially available high-pressure furnaces [18, 19]. In table 2, we have summarized the preparative conditions for 214 and related cuprate superconductors.

## 2.2. $\text{YBa}_2\text{Cu}_3\text{O}_7$ and other 123 cuprates

Superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  with the orthorhombic structure can be easily prepared by the ceramic method. Most of the investigations of the 123 compound,  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  have been carried out on the materials prepared by reacting  $\text{Y}_2\text{O}_3$  and  $\text{CuO}$  with  $\text{BaCO}_3$  [20, 21]. It is noteworthy that Rao *et al* [21] obtained monophasic  $\text{YBa}_2\text{Cu}_3\text{O}_7$  as the  $x=1.0$  member of the  $\text{Y}_{3-2x}\text{Ba}_{3+x}\text{Cu}_6\text{O}_{14}$  series. In the method employed for preparing  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , stoichiometric quantities of high-purity  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$  and  $\text{CuO}$  are ground thoroughly and heated initially in powder form around 1223 K for a period of 24 h. Following the calcination step, the powder is ground, pelletized and sintered at the same temperature for another 24 h. Finally, annealing is carried out in an atmosphere of oxygen around 773 K for 24 h to obtain the orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  phase showing 90 K superconductivity. Oxygen annealing has to be carried out below the orthorhombic tetragonal transition temperature ( $\sim 960$  K); tetragonal  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  ( $0.6 \leq x \leq 1.0$ ) is not superconducting. Intermittent grinding is necessary to obtain monophasic, homogeneous powders. This kind of complex heating schedule often gives rise to microscopic compositional inhomogeneities. Furthermore,  $\text{CO}_2$  released from the decomposition of  $\text{BaCO}_3$  can react with  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  to form non-superconducting

the evolution of  $\text{CO}_2$  during the synthesis is to use  $\text{BaO}_2$  instead of  $\text{BaCO}_3$ . Some of the impurities or side products in the preparation of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  are  $\text{BaCuO}_2$ ,  $\text{Y}_2\text{BaCuO}_5$  and  $\text{Y}_2\text{Cu}_2\text{O}_5$  [24]. The ternary phase diagram given in figure 1 illustrates the complexities of this cuprate system.

Using  $\text{BaO}_2$  as the starting material has two advantages. It has a lower decomposition temperature than  $\text{BaCO}_3$  and the 123 compound is therefore formed at relatively low temperatures.  $\text{BaO}_2$  acts as an internal oxygen source and the duration of annealing in an oxygen atmosphere is reduced to a considerable extent. Sharp superconducting transitions are observed in samples of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  made using  $\text{BaO}_2$ . Slight excess of copper in the ceramic method is reported to give cuprates with sharper transitions [25]. Preparation of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  is accomplished in a shorter period if one employs metal nitrates as the starting materials [13, 23]. In table 2, we present the conditions employed for preparing 123 cuprates by the ceramic method.

Other rare-earth cuprates of the 123 type,  $\text{LnBa}_2\text{Cu}_3\text{O}_{7-x}$  where  $\text{Ln} = \text{La, Nd, Sm, Eu, Gd, Dy, Ho, Er}$  and  $\text{Tm}$  (all with  $T_c$  values around 90 K) have also been prepared by the ceramic method [26, 27]. Oxygen annealing of these cuprates should also be carried out below the orthorhombic–tetragonal transition temperature [3]: La, 754 K; Nd, 837 K; Gd, 915 K; Er, 973 K; Yb, 976 K etc. Nearly 30% of Y can be substituted by Ca in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , retaining the basic crystal structure [28]; the  $T_c$  decreases with the increase in calcium content. Both La and Sr can be substituted at the Ba site in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  [29–31]. With La, monophasic products are obtained for  $0 \leq x \leq 1.0$  in  $\text{YBa}_{2-x}\text{La}_x\text{Cu}_3\text{O}_{7-x}$ , the  $T_c$  decreasing with increase in  $x$ . In the case of Sr substitution, monophasic products are obtained for  $0 \leq x \leq 1.25$  in  $\text{YBa}_{2-x}\text{Sr}_x\text{Cu}_3\text{O}_{7-x}$ ; high  $T_c$  is retained up to  $x=1.0$ . Ceramic methods have also been used to prepare  $\text{YBa}_2\text{Cu}_{3-x}\text{M}_x\text{O}_{7-x}$  solid solutions, where M generally stands for a transition element of the first series. In most

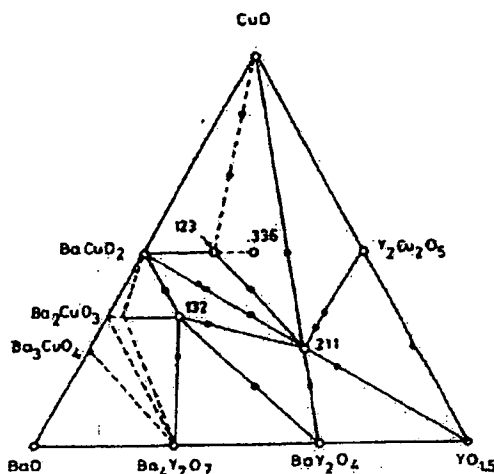


Figure 1. Phase diagram of the  $\text{Y}_2\text{O}_3$ – $\text{BaO}$ – $\text{CuO}$  system at 1220 K (from [24]).

Table 2. Preparative conditions for the synthesis of 214, 123, 124 and 247 type cuprates by the ceramic method.

Compound	Starting materials	Preparative conditions			Comments	$T_c$ (K)	Ref.
		Temp. (K)	Time	Gas			
$\text{La}_2\text{CuO}_{4-x}$	$\text{La}_2\text{O}_3, \text{CuO}$	1273 873	24 h 12-48 h	air $\text{O}_2$	3 kbar pressure	35 40	[15] [10]
$\text{La}_{1-x}\text{Sr}_x(\text{Ba}_y)\text{CuO}_4$	$\text{La}_2\text{O}_3, \text{Sr}/\text{BaCO}_3, \text{CuO}$	1393	36 h	$\text{O}_2$		32	[13]
$\text{La}_{1-x}\text{Sr}_x\text{CaCu}_2\text{O}_6$	$\text{La}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}, \text{Sr}/\text{Ba}(\text{NO}_3)_2, \text{Cu}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$	1273	20 h	air			
	$\text{La}_2\text{C}_2\text{O}_7, 10\text{H}_2\text{O}, \text{Sr}(\text{NO}_3)_2, \text{Ca}(\text{NO}_3)_2, 4\text{H}_2\text{O}, \text{CuO}$	973	18 h	$\text{O}_2$			
		1173	3 d	$\text{O}_2$			
		1168	3 d	$\text{O}_2$			
$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$	$\text{Y}_2\text{O}_3, \text{BaCO}_3, \text{CuO}$	1243	2 d	$\text{O}_2$	20 atm	60	[17]
		1223	2 d	air		88	[20]
	$\text{Y}_2\text{O}_3, \text{BaO}_2, \text{CuO}$	773	1 d	$\text{O}_2$		88	[22]
	$\text{Y}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}, \text{Ba}(\text{NO}_3)_2, \text{Cu}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$	723	1 d	air		90	[13]
$\text{YBa}_2\text{Cu}_4\text{O}_{13-x}$	$\text{Y}_2\text{O}_3, \text{BaCO}_3, \text{CuO}$	1173	18 h	$\text{O}_2$		81	[34]
		1223	—	$\text{O}_2$	400 bar	77	[35]
	$\text{Y}_2\text{O}_3, \text{Ba}(\text{NO}_3)_2, \text{CuO}$	1313	1 d	$\text{O}_2$	124 major phase + $\text{BaCuO}_2$ impurity	78	[36, 38]
	volumes of $\text{Na}_2\text{CO}_3$ or $\text{K}_2\text{CO}_3$ + equal volumes of $\text{Ba}(\text{NO}_3)_2, \text{CuO}$ + $0.2\text{M NaNO}_3$ or $\text{KNO}_3$ or $\text{Na}_2\text{O}_2$	1023 1073 1073	3 d 3 d 3 d	$\text{O}_2$ $\text{O}_2$ $\text{O}_2$	$\text{BaCuO}_2 + \text{Y}_2\text{BaCuO}_6$ 124 major phase + $\text{BaCuO}_2 + \text{Y}_2\text{BaCuO}_4$ 124 single phase	78 79 79	[38] [40] [39]
$\text{Y}_2\text{Ba}_2\text{Cu}_7\text{O}_{19-x}$	$\text{Y}_2\text{O}_3, \text{BaCO}_3, \text{CuO}$	1073	1 d	air	124 major phase + $\text{BaCuO}_2$	75	[39]
		1088	2 d	$\text{O}_2$	19 bar	90	[50]
	$\text{Y}_2\text{O}_3, \text{Ba}(\text{NO}_3)_2, \text{CuO}$	1088	10 d	$\text{O}_2$	Single phase	90	[36]
	$\text{Y}_2\text{O}_3, \text{Ba}(\text{NO}_3)_2, \text{CuO} + 0.2\text{M NaNO}_3$	1088	4 d	$\text{O}_2$	Single phase	90	[36]

\* Other rare-earth derivatives of the type  $\text{LnBa}_2\text{Cu}_3\text{O}_7$  are also prepared by this method. Oxygen annealing is carried out below the orthorhombic-tetragonal transition temperature [26, 27].

\* Other rare-earth derivatives of the type  $\text{LnBa}_2\text{Cu}_4\text{O}_{13}$  are obtained by a similar procedure [36, 40].

\* Other rare-earth derivatives of the type  $\text{Ln}_2\text{Ba}_2\text{Cu}_7\text{O}_{19}$  are prepared by a similar procedure [38, 39].

### 2.3. $\text{YBa}_2\text{Cu}_3\text{O}_x$ (124), $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ (247) and related cuprates

The first bulk synthesis of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  was reported by Karpinski *et al* [34] who heated the mixture of oxides at 1313 K, under an oxygen pressure of 400 bar. Synthesis of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  by the conventional ceramic method without the use of high oxygen pressure suffered from some limitations due to kinetic factors. Cava *et al* [35] found that additives such as alkali carbonates enhance the reaction rate. The procedure involves two steps. In the first step  $\text{Y}_2\text{O}_3$ ,  $\text{Ba}(\text{NO}_3)_2$  and  $\text{CuO}$  are mixed in the stoichiometric ratio and heated at 1023 K for 16–24 h in an oxygen atmosphere. In the second step, the pre-reacted powder is ground with an approximately equal volume of either  $\text{Na}_2\text{CO}_3$  or  $\text{K}_2\text{CO}_3$  powder and pellets of the resulting mixture are heated at 1073 K in flowing oxygen for 3 days. After the reaction, the product is washed with water to remove the excess alkali carbonate and dried by gentle heating in air. The product after this step has  $\text{YBa}_2\text{Cu}_3\text{O}_x$  as the majority phase ( $T_c$ , 77 K) with little  $\text{BaCuO}_2$  impurity. Other reaction rate enhancers such as  $\text{NaNO}_3$ ,  $\text{KNO}_3$ , dilute  $\text{HNO}_3$  and  $\text{Na}_2\text{O}_2$  have also been used successfully (in small quantities) to prepare  $\text{YBa}_2\text{Cu}_3\text{O}_x$  [36–38]. The 124 cuprate can also be prepared without the addition of a rate enhancer by the solid state reaction of  $\text{Y}_2\text{O}_3$ ,  $\text{BaCuO}_2$  and  $\text{CuO}$  at 1088 K in flowing oxygen [36]. Synthesis of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  from the solid state reaction between  $\text{YBa}_2\text{Cu}_3\text{O}_7$  and  $\text{CuO}$  in flowing oxygen has also been reported [39]. The synthesis of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  by the ceramic method generally takes a long time and requires repeated grinding and pelletizing.

Other rare-earth 124 cuprates,  $\text{LnBa}_2\text{Cu}_3\text{O}_x$  with  $\text{Ln} = \text{Eu, Gd, Dy, Ho}$  and  $\text{Er}$  have been prepared by the ceramic method under an oxygen pressure of 1 atm [36, 40]. The  $T_c$  of these cuprates decreases with the increasing ionic radius of the rare earth. Calcium can be substituted at the Y site up to 10% in  $\text{YBa}_2\text{Cu}_3\text{O}_x$ , and the  $T_c$  increases from 79 K to 87 K in such substituted  $\text{YBa}_2\text{Cu}_3\text{O}_x$  [41]. Lanthanum can be substituted for barium in  $\text{YBa}_2\text{Cu}_3\text{O}_x$  [42]. Single phases of  $\text{YBa}_{2-x}\text{La}_x\text{Cu}_3\text{O}_x$  have been obtained for  $0 \leq x \leq 0.4$  with the  $T_c$  decreasing with increase in  $x$ .

Extensive studies have been carried out on the synthesis of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  under high oxygen pressures [43, 44]. The  $P$ – $T$  phase diagram of 124, 123 and 247 cuprates is shown in figure 2. High-oxygen pressure synthesis essentially involves the solid state reaction followed by sintering under high oxygen pressures. The typical sintering temperature and the pressure at which synthesis of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  has been carried out are 1200 K and 120 atm of oxygen (for 8 h). By the use of high oxygen pressures [45], it is possible to prepare 124 compounds with other rare earths such as  $\text{Nd}$  and  $\text{Sm}$ , which is otherwise not possible under ambient pressures.

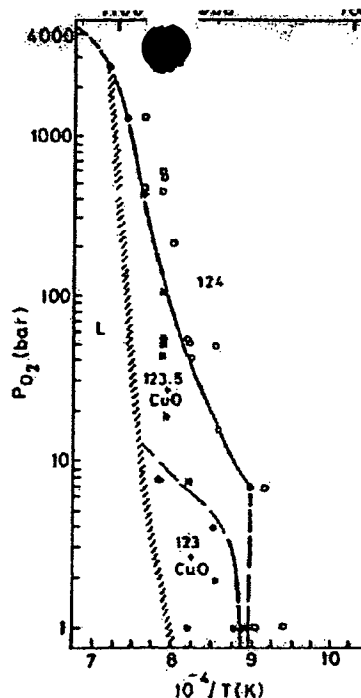


Figure 2. Phase diagram of the 124, 247 and 123 cuprates (from [43]).

A variety of substitutions has been carried out at the Y, Ba and Cu sites in  $\text{YBa}_2\text{Cu}_3\text{O}_x$  under high oxygen pressures. Yttrium can be substituted up to 10% by Ca in  $\text{YBa}_2\text{Cu}_3\text{O}_x$  giving a  $T_c$  of ~90 K [46]; 20% Ba has been substituted by Sr without affecting the  $T_c$  [47]. Single-phase iron-substituted  $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_x$  ( $0 \leq x \leq 0.05$ ) has been prepared at an oxygen pressure of 200 bar [48]; the  $T_c$  falls monotonically with increasing iron concentration.

Bordet *et al* [49] first reported the preparation of  $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$  under oxygen pressures of 100–200 bar. It was soon realized that  $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$  can be synthesized by the ceramic method under an oxygen pressure of 1 atm by a procedure similar to that employed for  $\text{YBa}_2\text{Cu}_3\text{O}_x$ , except for the difference in the sintering temperature [36]. There is a narrow stability region between 1123 K and 1143 K for the 247 cuprate to be synthesized under 1 atm oxygen pressure. The best sintering temperature at which the 247 cuprate is formed is 1133 K. Other rare-earth 247 cuprates,  $\text{Ln}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$  ( $\text{Ln} = \text{Dy, Er}$ ), can also be prepared by this method [36, 38]. About 5% of Y can be replaced by Ca in  $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ , and the  $T_c$  increases to 94 K [42]. Substitution of La at the Ba site is limited to ~10% in  $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$ , where the  $T_c$  decreases continuously with increasing lanthanum content [42].

Synthesis of 247 cuprates by the high-pressure oxygen method is generally carried out at 1203 K at an oxygen pressure of around 19 bar (for 8 h). This step is followed by slow cooling (typically  $5^\circ\text{C min}^{-1}$ ) to room temperature at the same pressure [50]. Other rare-earth 247 compounds,  $\text{Ln}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$  ( $\text{Ln} = \text{Eu, Gd, Dy, Ho}$

and Er), have been prepared in the oxygen pressure range of 14–35 bar [50]. Preparative conditions for the 124 and 247 cuprates are given in table 2.

#### 2.4. Bismuth cuprates

Although the ceramic method is widely employed for the synthesis of superconducting bismuth cuprates of the type  $\text{Bi}_2(\text{Ca}, \text{Sr})_{n-1}\text{Cu}_n\text{O}_{2n+4+\delta}$ , it is generally difficult to obtain monophasic compositions, due to various factors [51, 52]. Both thermodynamic and kinetic factors are clearly involved in determining the ease of formation as well as phasic purity of these cuprates. The  $n = 1$  member (2201) of the formula  $\text{Bi}_2\text{Sr}_2\text{CuO}_6$  appears to be stable around 1083 K and the  $n = 2$  member,  $\text{Bi}_2(\text{Ca}, \text{Sr})_2\text{Cu}_2\text{O}_8$  (2122) around 1113 K. The  $n = 3$  member,  $\text{Bi}_2(\text{Ca}, \text{Sr})_3\text{Cu}_3\text{O}_{10}$  (2223), can be obtained close to the melting point (1123 K) after heating for several days or even weeks. Of all the members of the  $\text{Bi}_2(\text{Ca}, \text{Sr})_{n-1}\text{Cu}_n\text{O}_{2n+4+\delta}$  family, the  $n = 2$  member (2122) seems to be most stable.  $\text{Bi}_2\text{O}_3$ , which is often used as one of the starting materials, melts at around 1103 K. Increasing the reaction temperature therefore leads to preferential loss of volatile  $\text{Bi}_2\text{O}_3$ . This results in micro-inhomogeneities and the presence of the unreacted oxides in the final product. Since these materials contain so many cations, partial reaction between various pairs of oxides leading to the formation of impurity phases in the final product cannot easily be avoided. A noteworthy structural feature of all these bismuth cuprates is the presence of superlattice modulation; the modulation has nothing to do with superconductivity.

Most of the above problems have been overcome by employing the matrix reaction method [53, 54]. This method reduces the number of reacting components and gives better products. In this method, synthesis is carried out by reacting the oxide matrix made from  $\text{CaCO}_3$ ,  $\text{SrCO}_3$  and  $\text{CuO}$  with  $\text{Bi}_2\text{O}_3$  in the temperature range of 1083–1123 K in air for a minimum period of 48 h. Quenching the samples in air from the sintering temperature or heating in a nitrogen atmosphere improves the superconducting properties of bismuth cuprates. The matrix reaction method yields monophasic  $n = 2$  (2122) and  $n = 3$  (2223) compositions showing  $T_c$  values of 85 K and 110 K respectively [55, 56]. Partial melting for a short period (~5 min) also favours the rapid formation of the  $n = 2$  (2122) and the  $n = 3$  (2223) members.

The  $n = 1$  member,  $\text{Bi}_2\text{Sr}_2\text{CuO}_6$ , showing  $T_c$  in the range 7–22 K is a rather complicated system and has two structurally different phases near the stoichiometric composition [51, 57–60]. Many workers have varied the Bi/Sr ratio and obtained single-phase materials with a  $T_c$  of 10 K at a composition which is strontium deficient,  $\text{Bi}_{2.1}\text{Sr}_{1.9}\text{CuO}_6$  [60, 61]. This cuprate is best prepared by reacting the oxides and/or carbonates of the constituent metals at 1123 K in air for extended periods of time. In figure 3 we show the phase diagram of the Bi–Sr–Cu–O system. The phase diagram of the

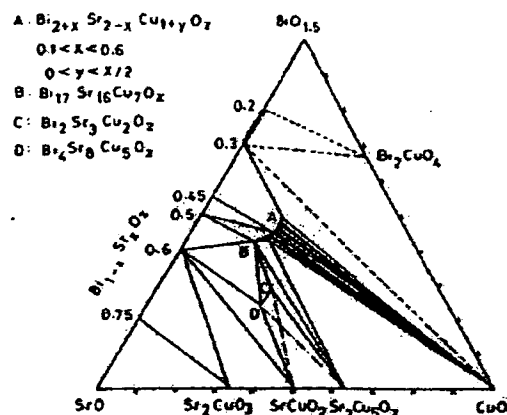


Figure 3. Phase diagram of the Bi–Sr–Cu–O system at 1110 K in air (from [60]).

$\text{Bi}_2\text{O}_3$ – $\text{SrO}$ – $\text{CaO}$ – $\text{CuO}$  system at a constant Cu content is shown in figure 4.

Substitution of a small amount of lead for bismuth results in good superconducting samples of  $n = 2$  (2122) and  $n = 3$  (2223) members. A number of workers have therefore preferred to synthesize both  $n = 2$  (2122) and  $n = 3$  (2223) members with substitution of lead up to 25% in place of bismuth [58, 63–66]. They are obtained either by direct reaction of oxides and/or carbonates of the cations or by the matrix reaction method.

Other than the matrix reaction method, melt quenching (glass route) [67, 68] and a semi-wet method [6] have been employed for the synthesis of superconducting bismuth cuprates. In the melt quenching method the mixture of starting materials (in the form of oxide and/or carbonates) is melted in a platinum or alumina crucible around 1473 K for a short period in air and then quenched in liquid nitrogen. The quenched specimens are given an annealing treatment around 1103 K in air to obtain the superconducting crystalline cuprates. This method has been shown to produce both  $n = 2$  (2122) and lead-doped  $n = 3$  (2223) members.

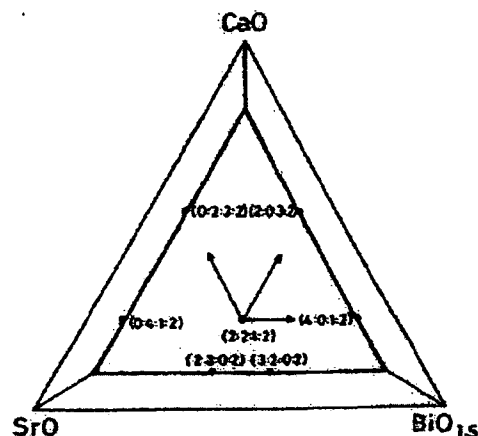


Figure 4. Section through the phase diagram of the  $\text{Bi}_2\text{O}_3$ – $\text{SrO}$ – $\text{CaO}$ – $\text{CuO}$  system at a constant CuO content of 28.6 mol% (from [62]).

semi-wet method involves the same reaction between two precursors which are precipitated separately. For example, in the preparation of  $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ , a precipitate of Pb, Sr and Ca (as carbonates) and one of Bi and Cu (as oxalates) are reacted at 1138 K in air for a minimum period of 72 h. The duration of the reaction for the formation of 2223 phase is drastically reduced by this method.

The starting composition of the reactant materials plays an important role in the synthesis of these cuprates. For example, strontium deficiency in the  $n = 1$  (2201) member favours monophasic compositions [59, 61]. Strontium deficiency also helps in obtaining a phase-pure  $n = 2$  (2122) member [70]. Starting with a 4:3:3:4 stoichiometry of Bi:Ca:Sr:Cu, it has been possible to obtain a monophasic 2122 member [54, 71]. The  $n = 3$  (2223) phase, on the other hand, is either obtained through the substitution of Bi by Pb (up to 25%) or by taking an excess of Ca and/or Cu [63–66, 72]. The problem of balancing between phase purity and high  $T_c$  of the cuprate gives rise to some difficulty in the synthesis of these cuprates. The coexistence of some of the members of the homologous series, especially in the form of polytypic intergrowths of different layered sequences, is also a problem. This problem is also encountered with thallium cuprates [73, 74].

The  $n = 4$  phase,  $\text{Bi}_{1.3}\text{Pb}_{0.5}\text{Ca}_3\text{Sr}_2\text{Cu}_4\text{O}_{12}$ , which was observed in an electron micrograph along with  $n = 3$  phase as an intergrowth, was synthesized in bulk by Rao *et al* [75] (with a small proportion of the  $n = 3$  phase) by the ceramic method. The  $n = 4$  phase has a slightly lower  $T_c$  (103 K), than the  $n = 3$  phase. This cuprate has also been prepared by Losch *et al* [75].

A variety of substitutions has been carried out in superconducting bismuth cuprates employing the ceramic method [58, 76–79]; some of them are noteworthy. For example, the simultaneous substitution of Bi by Pb and Sr by La in  $\text{Bi}_2\text{Sr}_2\text{CuO}_6$  results in a modulation-free superconductor of the formula  $\text{BiPbSr}_{1-x}\text{La}_x\text{CuO}_6$  with  $T_c$  increased to 24 K [77]. Similarly, co-substitution of Bi by Pb and Ca by Y in the  $n = 2$  member (2122) gives a modulation-free superconductor,  $\text{BiPbY}_{0.5}\text{Ca}_{0.5}\text{Sr}_2\text{Cu}_2\text{O}_8$  with a  $T_c$  of 85 K [77]. Rare-earth substitution for Ca in  $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$  causes the  $T_c$  to go up to 100 K without the introduction of the  $n = 3$  phase [58, 78]. As mentioned earlier, the  $n = 3$  phase is stabilized by the partial substitution of lead in place of bismuth [63–65]. Another significant discovery is the iodine intercalation of the Bi-2122 superconductor [80]. Intercalation does not greatly affect the superconducting properties of the material; clearly, superconductivity is confined to the two-dimensional  $\text{CuO}_2$  sheets in these materials.

Synthesis of a new series of superconducting cuprates of the general formula  $\text{Bi}_2\text{Sr}_2(\text{Ln}_{1-x}\text{Ce}_x)_2\text{Cu}_2\text{O}_{10}$  (Bi-2222 phase with  $\text{Ln} = \text{Sm, Eu, Gd}$ ) containing a fluorite-like  $(\text{Ln}_{1-x}\text{Ce}_x)_2\text{O}_2$  layer between the two  $\text{CuO}_2$  sheets has been possible by the ceramic method [81]. Partial substitution of bismuth by lead increases

stabilize the 2222 structure with other rare earths.

As mentioned earlier, one does not start with an exact stoichiometric composition to obtain the desired final product in the case of superconducting bismuth cuprates. Although structural studies (see for example [84]) indicate the presence of bismuth atoms over strontium and calcium sites as well, it is not possible to prescribe an exact initial composition to obtain the desired final stoichiometry. For example, starting from a nominal composition of  $(\text{Bi}_{0.7}\text{Pb}_{0.3})\text{SrCaCu}_2\text{O}_7$ , one ends up with the formation of the  $n = 3$  (2223) member [65]. Therefore, for the purpose of characterizing the various members of the superconducting bismuth cuprates, one starts with some arbitrary composition and varies the synthetic conditions suitably to obtain the desired final product in pure form. The actual compositions of the final cuprate are quite unexpected (e.g.  $\text{Bi}_{1.83}\text{Pb}_{0.30}\text{Sr}_{2.04}\text{Ca}_{1.60}\text{Cu}_3\text{O}_9$ ) as found from analytical electron microscopy [85]. In table 3 we have summarized the preparative conditions of all the members of  $\text{Bi}_2(\text{Ca, Sr})_{n+1}\text{Cu}_n\text{O}_{2n+4}$  family.

## 2.5. Thallium cuprates

The conventional ceramic method employed for the synthesis of 214, 123 and bismuth cuprates has to be modified in the case of thallium cuprates of the  $\text{Tl}_2\text{Ca}_{n-1}\text{Ba}_2\text{Cu}_n\text{O}_{2n+4}$ ,  $\text{TlCa}_{n-1}\text{Ba}_2\text{Cu}_n\text{O}_{2n+3}$  and  $\text{TlCa}_{n-1}\text{Sr}_2\text{Cu}_n\text{O}_{2n+3}$  families due to the toxicity and volatility of thallium oxide. In the early days, the reaction was carried out in an open furnace in air or oxygen atmosphere at high temperatures (1150–1180 K) for 5–10 min [86, 87]. In a typical procedure, the mixture of reactants in the form of a pellet was quickly introduced into the furnace maintained at the desired temperature. Since melt–solid reactions take place faster than solid–solid reactions, the product was formed quickly by this method [87]. Although this method requires a very short duration of heating, it results in the loss of thallium, leading to the danger of inhaling thallium oxide vapour. Some workers have taken certain precautions not to release the  $\text{Tl}_2\text{O}_3$  vapour into the open laboratory, but the method is still not recommended. Furthermore, the formation of the desired phase is not ensured under the open reaction conditions. Synthesis of thallium cuprates has therefore been carried out in closed containers (sealed tubes) by most workers. By this method, both polycrystalline samples and single crystals can be prepared, since the reaction is carried out over longer periods. Better control of stoichiometry, homogeneity of phases and the total avoidance of the inhalation of toxic thallium oxide vapours are some of the advantages of carrying out sealed tube reactions.

Closed reaction conditions have been achieved in different ways. The reactant mixture is sealed in gold [88] or silver tubes [89] or in a platinum [90] or nickel



Table 3. Preparative conditions for the synthesis of bismuth cuprates by the ceramic method.

Starting composition	Conditions*		Product	$T_c$ (K)	Ref.
	Temp. (K)	Time			
$\text{Bi}_2\text{Sr}_2\text{Cu}_2\text{O}_x$	1103	2 d	2201 major phase	20	[51]
$\text{Bi}_2\text{Sr}_2\text{CuO}_6$	1123	1 d	2201 major phase	8	[57]
$\text{Bi}_{2-x}\text{Sr}_{1+x}\text{CuO}_6$	1123	2 d	Single phase	10	[59, 61]
$\text{BiPbSr}_{1-x}\text{La}_x\text{CuO}_6$	1150	1 d	Single phase	24	[77]
$\text{Bi}_{1-x}\text{Ca}_x\text{Sr}_2\text{Cu}_2\text{O}_6$	1103	5 d	Single phase	85	[61]
$\text{Bi}_2\text{Ca}_{1-x}\text{Sr}_{1+x}\text{Cu}_2\text{O}_6$ <sup>b</sup>	1103	3 d	2122 major phase	80	[63]
$\text{Bi}_4\text{Ca}_3\text{Sr}_3\text{Cu}_4\text{O}_6$	1108	2 d	2122 single phase	85	[71]
$\text{Bi}_2\text{Sr}_{1-x}\text{Ca}_x\text{Cu}_2\text{O}_6$	1113	3 d	2122 single phase	85	[70]
$\text{BiPbSr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_2\text{O}_6$	1200	1 d	2122 single phase	85	[77]
$\text{Bi}_{1-x}\text{Pb}_x\text{Ca}_2\text{Sr}_2\text{Cu}_2\text{O}_6$ <sup>a</sup>	1140	5 d	2223 major phase	120	[55]
$\text{Bi}_{1-x}\text{Pb}_x\text{Ca}_{2-x}\text{Sr}_{1+x}\text{Cu}_2\text{O}_6$ <sup>b</sup>	1100	4 d	2223 major phase	105	[64]
$\text{Bi}_{1-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_2\text{O}_6$	1153	10 d	2223 single phase	110	[72]
$\text{Bi}_{0.7}\text{Pb}_{0.3}\text{SrCaCu}_{1.8}\text{O}_6$	1153	5 d	2223 major phase	105	[65]
$\text{BiCaSrCu}_2\text{O}_6$	1143	5 d	2223 major phase	120	[65]
$\text{Bi}_{3-x}\text{Pb}_x\text{Ca}_5\text{Sr}_4\text{Cu}_6\text{O}_6$	1133	5 d	2223 major phase	108	[64]
$\text{Bi}_2\text{Gd}_{1-x}\text{Ce}_x\text{Sr}_3\text{Cu}_2\text{O}_6$	1273	10 h	2222 single phase	30	[81]

<sup>a</sup> All the preparations carried out in air.<sup>b</sup> Obtained by matrix reaction method.

alloy (Inconel) container [91] closed tightly with a silver lid. Alternatively, the reactant mixture is taken in the form of a pellet, wrapped in a platinum [92] or gold [93] foil and then sealed in a quartz tube. This method has the advantage of carrying out the reaction under a vacuum. Some workers place the reactant pellet in an alumina crucible [94] which is then sealed in a quartz ampoule. Thallium-excess starting compositions have been employed by a few workers to compensate for the thallium loss during the reaction [95].

In the preparation of the thallium cuprates, the matrix reaction method is often employed. Here, a mixed oxide containing all the metal ions other than the volatile thallium oxide is first prepared by reacting the corresponding oxides and/or carbonates around 1200 K for 24 h in air [89, 96]. The freshly prepared mixed oxide is then taken with a calculated quantity of  $\text{Tl}_2\text{O}_3$  and heated at appropriate temperatures in a sealed tube. This method is desirable when a carbonate is used as the starting material. Some of the thallium cuprates have been prepared by a modified matrix method [97] wherein a thallium-containing precursor such as  $\text{Ba}_2\text{Tl}_2\text{O}_3$  is prepared first and then reacted with other components under closed conditions. Thallium-containing precursors are less volatile than  $\text{Tl}_2\text{O}_3$ , so that the loss of thallium is minimized during the preparation.

Thermodynamic and kinetic factors associated with the synthesis of thallium cuprates are complex due to the existence of various phases which are structurally related and which can therefore intergrow with one another. In fact, one of the common defects that occurs in the thallium cuprates is the presence of random intergrowths between the various layered phases [98]. Furthermore, many of the thallium, lead and bismuth superconductors are metastable phases which are entropy stabilized [99]. The temperature of the reac-

tion, the sintering time and the starting composition are therefore all crucial to obtaining monophasic products (table 4).

The effect of the starting composition is best illustrated by the formation of the  $n = 3$  phase of the bilayer thallium cuprates ( $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$ ). Synthesis of this compound starting from the stoichiometric mixture of the oxides corresponding to the ideal composition often yields the  $n = 2$  member of the family. It was found that starting with compositions rich in Ca and/or Cu (namely  $\text{TlCa}_2\text{BaCu}_3\text{O}_9$ ,  $\text{Tl}_2\text{Ca}_4\text{Ba}_2\text{Cu}_5\text{O}_{10}$ ) yielded a nearly pure  $n = 3$  phase [90, 98, 100]. The actual composition is, however, close to  $\text{Tl}_{1.7}\text{Ba}_2\text{Ca}_{2.3}\text{Cu}_3\text{O}_9$ . In the case of  $\text{TlCaBa}_2\text{Cu}_2\text{O}_7$  (1122) starting from a stoichiometric mixture of oxides corresponding to the ideal stoichiometry always yielded a mixture of 1122 and 2122 phases, the relative proportion of the two being dependent on the conditions. It has been demonstrated recently [101] that thallium-deficient compositions corresponding to  $\text{Tl}_{1-\delta}\text{CaBa}_2\text{Cu}_2\text{O}_7$  ( $\delta = 0.0$  to 0.3) yield better monophasic 1122 materials.

The thallium content of the material not only determines the number of Tl-O layers but controls the hole concentration. As mentioned earlier, one of the good starting compositions to obtain  $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$  (2223) is  $\text{TlCa}_2\text{BaCu}_3\text{O}_9$  (1313) which bears little relation to the composition of the final product. Another example is the formation of the  $n = 4$  phase,  $\text{TlCa}_4\text{Ba}_2\text{Cu}_4\text{O}_{10}$  (1324). Detailed studies [102] have shown that the 2223 phase formed initially transforms to the 1223 phase with an increase in the duration of heating. After prolonged sintering, the 1324 phase is formed at the expense of the 1223 phase. Similar transformations have also been observed in the formation process of  $\text{TlCa}_4\text{Ba}_2\text{Cu}_4\text{O}_{10}$  with five Cu-O layers [103].

The Sr analogue of  $\text{TlCa}_{n-1}\text{Ba}_2\text{Cu}_n\text{O}_{2n+3}$  cannot be prepared in pure form. However, they are stabilized by

Starting composition	Conditions			Product	$T_c$ (K)	Ref.
	Temp. (K)	Time	Gas			
$Tl_2Ba_2CuO_8$	1148	3 h	Sealed gold tubes	2201 single phase	84	[88]
$Tl_2CaBa_2Cu_2O_8$	1173	6 h	Sealed gold tubes	2122 single phase	98	[88]
	1150	3 h	Sealed silica ampoule	2122 single phase	95	[98]
$Tl_2Ca_4Ba_2Cu_5O_{10}$	1150	0.5 h	Sealed silica ampoule	2122 single phase	95	[98]
$Tl_4Ca_3Ba_4Cu_5O_{10}$	1150	0.5 h	Sealed silica ampoule	2122 single phase	95	[98]
$Tl_2Ca_2Ba_2Cu_3O_{10}$	1173	6 h	Sealed gold tubes	2223 major phase	105	[88]
	1123	20 min	Sealed silica ampoule	2223 major phase	106	[95]
	1103	12 h				
$TlCa_3BaCu_3O_7$	1153	3 h	Sealed silica ampoules	2223 major phase	125	[100]
$Tl_3CaBa_2Cu_3O_7$	1153	3 h	Sealed silica ampoules	2223 major phase	108	[100]
$TlBa_{1-x}La_{0.5}CuO_7$	1163	3 h	Sealed silica ampoules	1021 single phase	40	[111]
$TlSrLaCuO_5$	1170	2 h	Sealed silica ampoules	1021 single phase	40	[109]
$TlSr_{2-x}Nd_{0.5}Cu_2O_7$	1170	2 h	Sealed silica ampoules	1122 major phase	80	[110]
$TlCaBa_2Cu_2O_7$	1170	3 h	Sealed silica ampoules	1122 major phase + 2122 impurity	90	[101]
$Tl_{0.5}CaBa_2Cu_2O_7$	1170	3 h	Sealed silver tubes	1122 major phase	90	[101]
$(Tl_{0.5}Pb_{0.5})CaSr_2Cu_2O_7$	1170	3 h	Sealed silica ampoules	1122 single phase	90	[104]
$Tl(Ca_{0.5}Y_{0.5})Sr_2Cu_2O_7$	1170	3 h	Sealed silver tubes	1122 single phase	90	[92]
$TlCa_2Ba_2Cu_3O_9$	1163	6 h	Sealed silica ampoules	1223 single phase	115	[94]
$(Tl_{0.5}Pb_{0.5})Ca_2Sr_2Cu_3O_9$	1198	3-12 h	Sealed gold tubes	1223 single phase	122	[105]
$Tl_{0.5}Pb_{0.5}Sr_4Cu_3O_9$	1170	2 h	Sealed silica ampoules	1223 major phase	60	[110]

partly substituting Tl by Pb (or Bi) or Ca by yttrium or a trivalent rare earth [92, 104-107]. Thus,  $Tl_{0.5}Pb_{0.5}Ca_{n-1}Sr_2Cu_nO_{2n+3}$  shows a  $T_c$  of  $\sim 90$  K for  $n = 2$  and  $\sim 120$  K for  $n = 3$ .  $TlCa_{0.5}Y_{0.5}Sr_2Cu_2O_7$  also shows a  $T_c$  of 90 K. These cuprates in the Tl/Pb-Ca/Ln-Sr-Cu-O systems are prepared in a manner similar to the Tl-Ca-Ba-Cu-O system except that  $SrCO_3$  is used in place of  $BaCO_3$  or  $BaO_2$ .  $Sr_4Ti_2O_7$  has also been used as a starting material in some instances [97]. The  $n = 1$  member,  $TlM_2CuO_5$  ( $M = Sr$  or  $Ba$ ) is also stabilized by the substitution of Pb or Bi for Tl or a trivalent rare earth for Sr or Ba [108-111]. All these compounds showing a  $T_c$  of 40 K have been prepared by the matrix reaction method.

Single thallium layer cuprates of the general formula  $Tl_{1-x}A_{2-x}Ln_2Cu_2O_9$  with  $A = Sr, Ba$ ;  $Ln = Pr$  (Nd, Ce) as well as  $Tl_{0.5}Pb_{0.5}(Ln_{1-x}Ce_x)_2Sr_2Cu_2O_9$  ( $Ln = Pr, Gd$ ) with a fluorite-type  $Ln_2O_3$  layer have been prepared by the ceramic method [112, 113]. The as-prepared materials are semiconductors. It has been shown by Liu *et al* [114] that annealing  $TlBa_2(Eu, Ce)_2Cu_2O_9$  (1222 phase) under an oxygen pressure of 100 bar induces superconductivity with a  $T_c$  of  $\sim 40$  K.

As in the case of bismuth cuprates, the final composition of thallium cuprates is unlikely to reflect the composition of the starting mixture. Structural studies [99, 115] have shown that there is cation disorder between Tl and Ca/Sr sites. Therefore, in order to obtain a superconducting composition corresponding to a particular copper content, one has to start with various arbitrary compositions and vary the synthesis conditions. The actual composition of the final product can be quite unexpected (e.g.  $Tl_{1.83}Ba_2Ca_{1.44}Cu_3O_9$  or  $Tl_{1.86}Ba_{2.01}CuO_9$ ) as shown by analytical electron microscopy [85]. In table 4 we have listed the pre-

parative conditions employed for the synthesis of thallium cuprates by the ceramic method.

## 2.6. Lead cuprates

The conditions for the synthesis of superconducting lead cuprates are more stringent than for the other copper oxide superconductors. Direct synthesis of members of the  $Pb_2Sr_2(Ln, Ca)Cu_3O_{8+x}$  ( $Ln = Y$  or rare earth) family by the reaction of the component metal oxides or carbonates in air or oxygen at temperatures below 1173 K is not possible because of the high stability of  $SrPbO_3$ -related perovskite oxides. Preferential loss of the more volatile  $PbO$  leads to micro-inhomogeneities. Furthermore, Pb in these compounds is in the 2+ state while part of the Cu is in the 1+ state. Synthesis has therefore to be carried out under mildly reducing conditions, typically in an atmosphere of  $N_2$  containing 1%  $O_2$ . The most common method that has been employed for the synthesis of these lead cuprates is the matrix reaction method [116]. For  $Pb_2Sr_2(Ln, Ca)Cu_3O_{8+x}$  ( $Ln = Y$  or rare earth), a mixed oxide containing all the metal ions except Pb is made by reacting  $SrCO_3$ ,  $Ln_2O_3$  or  $Y_2O_3$ ,  $CaCO_3$  and  $CuO$  in the appropriate ratios around 1223 K in air for 16 h. The mixed oxide is then taken with an appropriate amount of  $PbO$ , ground thoroughly, pelletized and heated in the 1133-1198 K range in a flowing stream of nitrogen containing 1%  $O_2$  for periods between 1 and 16 h. Generally, short reaction times and quenching the product from the sintering temperatures into liquid nitrogen in the same atmosphere gives better-quality samples. Even though this is the common method for preparing  $Pb_2Sr_2(Ln, Ca)Cu_3O_{8+x}$ , it is not always easy to obtain samples exhibiting good, reproducible

superconducting properties. The lead cuprates from the method described above generally show broad transitions in the  $R-T$  curves with negative temperature coefficients of resistance above  $T_c$ .

Studies of the dependence of  $T_c$  on the calcium concentration in the  $\text{Pb}_2\text{Sr}_2\text{Y}_{1-x}\text{Ca}_x\text{Cu}_3\text{O}_{8+x}$  system [117] have shown that heating the samples near the melting point between 1198 and 1228 K for 2 h and post-annealing in flowing nitrogen gas at a temperature between 673 and 773 K improves the superconducting properties of the samples dramatically. Direct one-step synthesis has been achieved [118] by reacting the metal oxides in sealed gold tubes around 1223 K. An alternative route to the direct synthesis from metal oxides and/or carbonates has also been demonstrated [119]. Superconductivity near 70 K has been reported in Ca-free  $\text{Pb}_2\text{Sr}_2\text{LnCu}_3\text{O}_{8+x}$  ( $\text{Ln} = \text{Y}$  or rare earth) employing the vacuum annealing procedure [120]. Substitution of Pb by Bi in  $\text{Pb}_2\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_{8+x}$  has also been carried out by the ceramic method [121]. About 30% of Pb can be substituted by Bi, and such a substitution increases the  $T_c$  up to 100 K. The  $n = 0$  member of the  $\text{Pb}_2\text{Sr}_2(\text{Ca}_{1-x}\text{Ln}_x)\text{Cu}_{2+2x}\text{O}_{6+2x}$  series (namely  $\text{Pb}_2(\text{SrLa})\text{Cu}_2\text{O}_{6+x}$ ) has been prepared successfully by this matrix reaction method [122].

Unlike the 2213-type lead cuprates, superconducting 1212-type lead cuprates of the formula  $(\text{Pb}_{0.5}\text{Cu}_{0.5})\text{Sr}_2(\text{Y}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_{7-x}$  are synthesized in an oxidizing atmosphere. Several authors have reported direct synthesis as well as reactions under closed conditions [123–127]. In the direct synthesis of these cuprates, care is taken to prevent the loss of Pb by wrapping pellets in gold or platinum foil [127]. Rouillon *et al* [125, 126] have reported the synthesis of 1212 lead cuprates by the direct reaction of the component oxides in evacuated silica ampoules. This method has

the advantage of adjusting the oxygen partial pressure required for the synthesis. Both 2213-type and 1212-type lead cuprates have been prepared using the nitrates of the metal ions as the starting materials [128]. Although this procedure yields 2213 or 1212 phases in a single step, the product obtained always has impurities such as  $\text{Y}_2\text{O}_3$ ,  $\text{CuO}$  etc.

A superconducting lead cuprate of the formula  $(\text{Pb}, \text{Cu})(\text{Eu}, \text{Ce})_2(\text{Sr}, \text{Eu})_2\text{Cu}_2\text{O}_9$  (1222 phase) containing a fluorite layer has been prepared by the direct reaction of the component metal oxides at 1273 K in oxygen atmosphere [129].

High-pressure ceramic synthesis has been employed to prepare lead cuprates of the 1212 type [130, 131]. In order to prepare  $\text{Pb}_{0.5}\text{Cu}_{0.5}\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_2\text{O}_{7-x}$ , sintering is carried out at 1213 K for 15 h under an oxygen pressure of 100 bar followed by fast cooling to 373 K. The samples obtained from high-pressure oxygen treatment show higher  $T_c$ s than those processed at 1 bar pressure of oxygen. Substitution of Y by other rare earths has been possible by this high-oxygen-pressure method [131]. All the rare-earth substituted compounds are superconducting with  $T_c$ s in the 50–70 K range. The  $T_c$  decreases with increase in the size of the rare earth. In table 5 we summarize the conditions for the synthesis of the various lead cuprates by the ceramic method.

## 2.7 Electron-doped superconductors

All the cuprates discussed till now are hole superconductors. Synthesis of electron-doped cuprate superconductors of the type  $\text{Ln}_{1-x}\text{M}_x\text{CuO}_{4-x}$  ( $\text{Ln} = \text{Nd}, \text{Pr}, \text{Sm}, \text{Eu}$ ;  $\text{M} = \text{Ce}, \text{Th}$ ), possessing the  $T'$  structure, is generally achieved by the ceramic method [132–134]. The conditions of synthesis are more stringent since the

Table 5. Conditions for the synthesis of lead cuprates by the ceramic method.

Compound	Starting materials	Conditions			Comments	$T_c$ (K)	Ref.
		Temp. (K)	Time	Gas			
$\text{Pb}_2\text{Sr}_2\text{Ca}_{0.5}\text{Y}_{0.5}\text{Cu}_3\text{O}_{8-x}$	$\text{PbO} + \text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_{8-x}$	1143	1–16 h	$\text{N}_2 + 1\% \text{O}_2$		78	[116]
	$\text{Cu}_2\text{O}_3$ matrix						
	$\text{PbO}, \text{PbO}_2, \text{CaO}_2$	1223	12–48 h		Sealed gold tubes	78	[118]
	$\text{SrO}_2, \text{Y}_2\text{O}_3, \text{CuO}$	1073	15 h	air			
	$\text{PbO}, \text{SrCO}_3, \text{Y}_2\text{O}_3$	1173	2 h	air			
$\text{Pb}_2\text{Sr}_2\text{La}_{1.2}\text{Cu}_2\text{O}_{8+x}$	$\text{CaCO}_3, \text{CuO}$	1073	1–5 h	$\text{N}_2$		78	[119]
	$\text{PbO}, \text{La}_2\text{O}_3$	1063	6 h	$\text{N}_2$	2202 major phase + $\text{Pb}_2\text{LaCu}_{0.5}\text{O}_x$ impurity	28	[122]
	$\text{Sr}_2\text{CuO}_3, \text{CuO}$						
	$\text{PbO}, \text{SrCO}_3, \text{La}_2\text{O}_3$	1073	5 h	air			
$(\text{Pb}_{0.5}\text{Cu}_{0.5})\text{SrLaCuO}_4$	$\text{CuO}$	1273	2 h	$\text{O}_2$		25	[123]
	$\text{PbO}, \text{SrCO}_3, \text{Y}_2\text{O}_3$	1123	10 h	air			
	$\text{CaCO}_3, \text{CuO}$	1273	1 h	$\text{O}_2$			
	$\text{PbO} + \text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_{2.5}\text{O}_7$	1243	3 h	$\text{O}_2$	1212 major phase + $\text{Sr}_2\text{PbCuO}_{1.5}$ impurity	50	[124]
$(\text{Pb}_{0.5}\text{Sr}_{0.5})\text{Sr}_2(\text{Y}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_7$	$\text{Cu}_{2.5}\text{O}_7$ matrix				1212 major phase + $\text{Sr}_2\text{PbCuO}_{1.5}$ impurity	47	[127]
	$\text{PbO}, \text{PbO}_2, \text{Sr}_2\text{CuO}_3$	1108–1223	1–10 h		Evacuated silica tubes	100	[125]
	$\text{Y}_2\text{O}_3, \text{CaO}_2, \text{Cu}_2\text{O}, \text{CuO}$						
	$\text{PbO}_2, \text{PbO}, \text{SrO}_2$	1108–1223	1–10 h		Evacuated silica tubes	80	[126]
$(\text{Pb}_{0.5}\text{Cu}_{0.5})\text{Sr}_2(\text{Y}_{0.5}\text{Ca}_{0.5})\text{Cu}_2\text{O}_7$	$\text{SrCuO}_2, \text{Y}_2\text{O}_3, \text{CaO}, \text{CuO}$						
	$\text{PbO}, \text{SrCO}_3, \text{Eu}_2\text{O}_3$	1123	10 h	air	Single phase	25	[129]
	$\text{CeO}_2, \text{CuO}$	1323	1 h	$\text{O}_2$	1222		

material, by making sure that extra electron donated by  $Ce^{4+}$  or  $Th^{4+}$  does not increase the oxygen content of the cuprate. For this reason, samples after calcination and sintering at 1323 K in air (for 24 h) are annealed in a reducing atmosphere (typically Ar,  $N_2$  or dilute  $H_2$ ) at 1173 K to achieve superconductivity. Samples prepared in this manner show a negative temperature coefficient of resistance above  $T_c$  in the  $R$ - $T$  curves; the resistivity drop at  $T_c$  is also not sharp. An alternative synthetic route involves the reaction of pre-reacted  $NdCeO_{3.5}$  material with the required amounts of  $Nd_2O_3$  and  $CuO$  at 1253 K for a minimum period of 48 h in flowing oxygen [135]. The samples are then rapidly quenched from 1253 K in an argon atmosphere to achieve superconductivity. This procedure eliminates the slow diffusion of Ce throughout the  $Nd_2CuO_{4-x}$  host and gives uniform concentrations of cerium and oxygen. Samples obtained from this route show a sharp transition at 21 K.

Superconductivity with a  $T_c$  of 25 K is induced by doping fluorine for oxygen in  $Nd_2CuO_4$ . This has been accomplished by taking  $NdF_3$  as one of the initial reactants [136]. Substitution of either Ga or In for copper in non-superconducting  $Nd_{2-x}Ce_xCuO_{4-x}$  also induces superconductivity [137, 138].

### 2.8. Infinite-layer cuprates

Discovery of superconductivity in cuprates containing infinite  $CuO_2$  layers has been of great importance in understanding the phenomenon. Very high pressures have been employed for obtaining the infinite-layer cuprates. Both hole-doped (e.g.  $Ca_{1-x}Sr_xCuO_2$ ) and electron-doped ( $Sr_{1-x}Nd_xCuO_2$ ) infinite-layer cuprate superconductors with a maximum  $T_c$  of 110 K have been reported [139-142]. Infinite-layered cuprates of the type  $(Ba, Sr)CuO_2$ ,  $(Ca, Sr)CuO_2$  are synthesized in an oxidizing atmosphere under high hydrostatic pressure [139, 140, 142]. Electron-doped  $Sr_{0.88}Nd_{0.14}CuO_2$  is also prepared under high hydrostatic pressures [141]. Metal nitrates are generally used as the starting materials since carbonates of Ba, Sr and Ca have high decomposition temperatures. After decomposing the metal nitrates at around 873-1123 K in air, the product is subjected to high pressure to obtain the superconducting phases.  $Sr_{0.88}Nd_{0.14}CuO_2$ , which superconducts at 40 K, is made under a hydrostatic pressure of 25 kbar at 1273 K. Superconducting  $(Ca, Sr)CuO_2$  is prepared at 1273 K under 6 GPa pressure. Deficiency of Sr and Ca as well as the oxidizing atmosphere make this phase superconducting, and the oxidizing atmosphere is provided by heating a capsule containing  $KClO_4$  along with the sample. This cuprate has a  $T_c$  (onset) of 110 K.

### 3. Coprecipitation and precursor methods

Coprecipitation involves the separation of a solid containing various ionic species chemically bound to one

another. Coprecipitation can result in the formation of crystalline or amorphous solids. Coprecipitation of well defined stoichiometry with respect to the metal ions is obtained only when the following conditions are satisfied.

(i) The precipitating agent is a multivalent organic compound which can coordinate with more than one metal ion, and the precipitation rate is fast.

(ii) The solid precipitating out of the solution should be really insoluble in the mother liquor.

The anions generally preferred for coprecipitation of oxidic materials are carbonates, oxalates, citrates etc. The same is true of high- $T_c$  cuprates. The precipitates in some instances could be genuine precursors or solid solutions [5, 6]. It is well known that precursor solid solutions drastically bring down diffusion distances for the cations and facilitate reactions in the solid state. We shall not distinguish precursor solid solutions precipitated from solutions from other precursors in this discussion.

The precipitates (carbonate, oxalate etc) are heated at appropriate temperatures in a suitable atmosphere to obtain the desired cuprate. Some of the advantages of the coprecipitation technique over the ceramic method are an homogeneous distribution of components, a decrease in the reaction temperatures and of the duration of annealing, a higher density and a lower particle size of the final product. The major drawback of this route is the control over the stoichiometry of the final product.

#### 3.1. $La_{2-x}Sr_xCuO_4$

La, Sr and Cu in  $La_{2-x}Sr_xCuO_4$  are readily coprecipitated as carbonates [11, 12, 143]. For this purpose the required quantities of the various metal nitrates are dissolved together in distilled water. Alternatively, the corresponding oxides are dissolved in nitric acid to give a nitrate solution and the pH of the solution is adjusted to 7-8 by the addition of KOH solution. A solution of  $K_2CO_3$  of appropriate strength is then slowly added under stirring to give a light blue precipitate which is thoroughly washed. The precipitate is dried at 420 K and calcined at 1070 K for 8 h in air. The resulting black powder is ground and pelletized and sintered at 1270 K for 16 h in air to obtain monophasic  $La_{1.85}Sr_{0.15}CuO_4$ , superconducting at 35 K.

Instead of as carbonate, the metal ions are also readily precipitated as oxalate by the addition of either oxalic acid or potassium oxalate to the solution of metal nitrates [11, 12, 144, 145]. The precipitated oxalate is then decomposed to obtain the cuprate. This method has certain disadvantages:

(i)  $La^{3+}$  in the presence of an alkali metal oxalate first yields lanthanum oxalate which further reacts with the precipitating agent to give a double salt. Control of stoichiometry therefore becomes difficult, leading to multiphasic products.

(ii) The relative solubilities of some of the oxalates also pose difficulties. For example,  $\text{SrC}_2\text{O}_4$  is nearly four times more soluble than  $\text{SrCO}_3$ .

### 3.2. $\text{YBa}_2\text{Cu}_3\text{O}_7$

$\text{YBa}_2\text{Cu}_3\text{O}_7$  and related 123 compounds can be obtained via coprecipitation of the component metals (from a nitrate solution) as a formate [146, 147], acetate [148], oxalate [12, 149–156], hyponitrite [157] or hydroxycarbonate [158, 159]. Some of these precipitates could be genuine precursor compounds as is indeed the case with the hyponitrite.

In oxalate coprecipitation [12, 149–152], oxalic acid solution of appropriate concentration is added to an aqueous solution of mixture of nitrates of Y, Ba and Cu and the pH of the solution is adjusted to 7.5 (by dilute  $\text{NH}_3$ ). The pale green slurry thus formed is digested for 1 h, filtered and dried. The oxalate is converted to orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  by heating at 1053 K in air for 5 days followed by oxygenation at 723 K. This procedure, even though successful in making superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  in small particulate form, often results in undesirable stoichiometry because of the moderate solubility of barium oxalate. Furthermore, rare-earth ions in the presence of ammonium oxalate give a double salt with the excess oxalate which competes with the precipitation of copper and barium oxalates. These difficulties can be overcome either by taking a known excess (wt%) of barium and copper or by using triethylammonium oxalate as the precipitant in aqueous ethanol medium [153–155]. The alcoholic medium decreases the solubility of barium oxalate and the pH of the solution is controlled *in situ*.

A better method of homogeneous coprecipitation of oxalates is that of Liu *et al.* [156] using urea and oxalic acid. Urea, on heating, is hydrolysed liberating  $\text{CO}_2$  and  $\text{NH}_3$ , and thus gradually adjusting the pH throughout the solution. The  $\text{CO}_2$  liberated controls the bumping of the solution during digestion. The oxalate coprecipitation route is widely described in the literature. The reactive powders obtained by the oxalate coprecipitation method decrease the sintering temperature. The formation of  $\text{BaCO}_3$  in the intermediate calcinating step makes it difficult to obtain  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  in pure form.

Complete avoidance of the formation of  $\text{BaCO}_3$  during the synthesis is possible using the hyponitrite precursor [157]. The hyponitrite precursor is obtained from a nitrate solution of Y, Ba and Cu ions by the addition of an aqueous  $\text{Na}_2\text{N}_2\text{O}_2$  solution. The precipitate is converted into superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  by heating at around 973 K in an argon atmosphere, followed by oxygen annealing at 673 K. Although this route provides a convenient means of obtaining the 123 cuprate at much lower temperatures than with other methods, there is a possibility of contamination of alkali metal ions during the course of the precipitation.

$\text{YBa}_2\text{Cu}_3\text{O}_7$  can also be prepared by the hydroxycarbonate method [158, 159]. Here,  $\text{KOH}$  and  $\text{K}_2\text{CO}_3$

are employed to precipitate copper as the hydroxide and Y and Ba as the carbonates in the pH range of 7–8. By employing  $\text{NaOH}$  and  $\text{Na}_2\text{CO}_3$ , complete precipitation as hydroxycarbonate is attained at a pH of  $\sim 13$ . The product from the above two procedures is homogeneous, showing sharp onset of superconductivity at 92 K. The possibility of contamination by alkali metal ions cannot, however, be avoided.

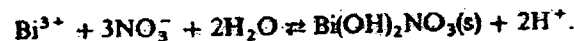
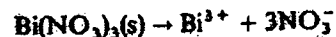
### 3.3. $\text{YBa}_2\text{Cu}_4\text{O}_8$

$\text{YBa}_2\text{Cu}_4\text{O}_8$  can be prepared by the oxalate route [160] wherein the solution of Y, Ba and Cu nitrates in water is added dropwise into oxalic acid–triethylamine solution under stirring. Complete precipitation of Y, Ba and Cu with the desired stoichiometry of 1:2:4 is achieved in the pH range of 9.3–11.3. The precipitated oxalates are filtered and dried in air at 393 K. The solid obtained is then heated in the form of pellets at 1078 K in flowing oxygen for 2–4 days. The product after quenching in air shows the 124 phase as the major product with a  $T_c$  of 79 K.

An alternative coprecipitation route for the synthesis of  $\text{YBa}_2\text{Cu}_4\text{O}_8$  is the method of Chen *et al.* [161] in which the aqueous nitrate solution of the constituent metal ions is mixed with 8-hydroxyquinoline–triethylamine solution. The precipitated oxine is filtered, washed, dried and sintered at 1088 K in oxygen for 3 days to yield phase-pure  $\text{YBa}_2\text{Cu}_4\text{O}_8$  showing a  $T_c$  of 80 K. Ethylenediaminetetraacetic acid [161] as well as carbonate routes [162] have also been employed for the preparation of  $\text{YBa}_2\text{Cu}_4\text{O}_8$ . Coprecipitation using triethylammonium oxalate has been exploited for substituting Sr in place of Ba in  $\text{YBa}_2\text{Cu}_4\text{O}_8$  [163].

### 3.4. Bismuth cuprates

Very few coprecipitation studies have been carried out on the preparation of bismuth cuprates. One reason may be that despite the good sample homogeneity generally obtained through solution methods, the chemistry of bismuth cuprates is rather complex. It is not that easy to find compounds of all the constituent metal ions soluble in a common solvent; controlling the stoichiometry in these cuprates is also difficult in the coprecipitation procedure. Furthermore, bismuth nitrate, which is often used as one of the starting materials, decomposes in cold water to a basic nitrate precipitate as given by



This problem can be overcome to some extent by preparing the nitrate solution of bismuth in nitric acid or by starting with bismuth acetate instead of the nitrate.

Bidentate ligands such as the oxalate are found to react more rapidly than multidentate ligands such as citric acid [164–174] in the coprecipitation process. Complexes of oxalic acid are also more stable than

the stoichiometry because of the relative solubility of  $\text{BiC}_2\text{O}_4$  or  $\text{SrC}_2\text{O}_4$ .

A straightforward oxalate coprecipitation is achieved by dissolving the acetates of Bi, Ca, Sr and Cu in glacial acetic acid and then adding excess oxalic acid to the solution [164]. The oxalate precipitate is dried and decomposed at around 1073 K in air and processed in the 1103–1123 K range for periods ranging from 24 h to 4 days, depending on the starting composition. The  $n = 2$  (2122) member obtained by this procedure shows zero resistance at 83 K. In another procedure reported by Zhang *et al* [165], first the Sr/Ca/Cu nitrate solutions are mixed in the required molar ratio. Into this solution is poured a solution of bismuth nitrate prepared in nitric acid along with oxalic acid. The complete precipitation occurs at a pH of around 5 (attained by the addition of aqueous NaOH). This process involves the possibility of contamination of sodium ions; this has been circumvented by using  $\text{N}(\text{CH}_3)_4\text{OH}$  to adjust the pH of the solution [166] and complete precipitation of the oxalates occurs at a pH of 12. All these procedures, however, produce mixed-phase samples.

For the preparation of the monophasic lead-doped  $n = 3$  member (2223), oxalate coprecipitation has been found effective [167–174]. In the procedure reported by Chiang *et al* [171], the molar ratio of the chelating agent (oxalic acid) and the nitrate anions (from the metal nitrate solutions) is fixed at 0.5 and the pH, adjusted by  $\text{NH}_4\text{OH}$  solution, at which complete precipitation occurs is 6.7. The product from this method,  $\text{Bi}_{1.4}\text{Pb}_{0.6}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ , after sintering at 1133 K in air for 72 h, shows a  $T_c$  of 110 K.

Coprecipitation as oxalates to prepare the lead-doped  $n = 3$  member (2223) has been achieved from an ethylene glycol medium using triethylammonium oxalate and oxalic acid [172]. A more easily controlled and reproducible oxalate coprecipitation procedure appears to be that of Shei *et al* [173] where in a mixture of triethylamine and oxalic acid is employed. The advantage of using triethylamine is that it has a higher basicity and a lower complexing ability towards  $\text{Cu(II)}$  than has ammonia. Control of the stoichiometry of the final product is therefore better obtained with this procedure; precipitation occurs in the pH range 1.5–2.2. The coprecipitated oxalates sintered at 1133 K in air for a minimum period of 72 h give monophasic  $\text{Bi}_{1.4}\text{Pb}_{0.6}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  with a  $T_c$  of 110 K. It is possible to avoid adjusting the pH in the coprecipitation of oxalates [174]. The procedure involves coprecipitating the oxalates from dilute acetate solutions instead of from nitrate solutions. The oxalates are then converted to nearly phase-pure  $\text{Bi}_{1.4}\text{Pb}_{0.6}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  ( $T_c$  of 106 K) by sintering at 1123 K in air for 160 h.

Carbonate coprecipitation has also been carried out for the synthesis of superconducting bismuth cuprates [175, 176], but the method does not yield monophasic products.

Coprecipitation of  $n = 3$  member cuprates from aqueous solutions as oxalates is hindered by the solubility of thallium oxalate. However, Bernhard and Gritzner [177] have found that complete coprecipitation as oxalates can be achieved by starting with thallium acetate in glacial acetic acid medium. In the procedure reported for the preparation of the  $n = 3$  member (2223), stoichiometric amounts of thallium acetate,  $\text{CaCO}_3$ ,  $\text{BaCO}_3$  and copper acetate are dissolved in water containing glacial acetic acid. The solution containing all the cations is then added to a solution of oxalic acid (excess) under stirring. The precipitate, after digestion for 1 h, is filtered, washed and dried. The oxalates are heated in the form of pellets (wrapped in gold foil) at around 1173 K for 6 min in an oxygen atmosphere. The product after annealing in the same atmosphere shows 2223 as the major phase with a  $T_c$  of 118 K.

### 3.6. Lead cuprates

Carbonate coprecipitation is found to be satisfactory for the synthesis of representative members of superconducting lead cuprates [128] of 2213 and 1212 types, namely  $\text{Pb}_2\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_{8+x}$  and  $\text{Pb}_{0.5}\text{Sr}_{0.5}\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_2\text{O}_{7-x}$ . Coprecipitation as carbonates has been achieved by adding the nitrate solution of the constituent metal ions to an aqueous solution of sodium carbonate (in excess) under constant stirring. The carbonate precipitate thus obtained is washed and dried. The decomposed powder is heated in the form of pellets around 1153 K in a suitable atmosphere.  $\text{Pb}_2\text{Sr}_2\text{Ca}_{0.5}\text{Y}_{0.5}\text{Cu}_3\text{O}_{8+x}$  obtained by this method after heating for 4 h in nitrogen containing 1%  $\text{O}_2$  showed 2213 as the major phase ( $T_c \sim 74$  K) with impurities such as  $\text{Y}_2\text{O}_3$ ,  $\text{CuO}$ . The 1212 phase obtained after heating in oxygen at 1153 K for 12 h showed a broad transition with a  $T_c$  (onset) of 100 K. This method has the advantage of single heating rather than the multistep procedures required in the other methods.

## 4. Sol-gel process

The sol-gel process is employed in order to get homogeneous mixing of cations on an atomic scale so that the solid state reaction occurs to completion in a short time and at the lowest possible temperature. The term sol often refers to a suspension or dispersion of discrete colloidal particles, while a gel represents a colloidal or polymeric solid containing a fluid component which has the internal network structure wherein both the solid and the fluid components are highly dispersed. In the sol-gel process a concentrated sol of the reactant oxides or hydroxides is converted to a semi-rigid gel by removing the solvent. The dry gel is heated at an appropriate

temperature to obtain the product. Most of the reactions in the sol-gel process occur via hydrolysis and polycondensation.

Two different routes for the sol-gel process are usually described in the literature for the synthesis of high- $T_c$  cuprate superconductors:

- (i) Via molecular precursors (e.g. metal alkoxides) in organic medium;
- (ii) Via ionic precursors in aqueous medium (citrate gel process).

The purity, microstructure and physical properties of the product are controlled by varying the precursor, solvent, pH, firing temperatures and atmosphere of heat treatment.

#### 4.1. 214 Cuprates

Superconducting 214 compounds are prepared both by means of organometallic precursor [178] and by the citrate gel process [11]. Lanthanum 2,4-pentanedionate, barium 2,4-pentanedionate and copper (II) ethyl hexanoate are mixed at room temperature in the appropriate ratios in methoxyethanol medium to obtain the organometallic precursor. After vigorous stirring at room temperature, the precursor gel is converted to monophasic  $\text{La}_{1-x}\text{Ba}_x\text{CuO}_4$  ( $T_c$  23 K) by firing at 873 K in oxygen.

In the citrate gel process, a mixture of citric acid and ethylene glycol is added to the solution containing the required quantities of metal nitrates. The resulting solution is vigorously stirred and heated around 393 K. During this process, oxides of nitrogen evolve, resulting in a viscous gel. The gel is decomposed at 673 K in air and the resulting black powder is then given the necessary heat treatment to obtain the superconducting oxide.

#### 4.2. $\text{YBa}_2\text{Cu}_3\text{O}_7$

In the case of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , the alkoxide precursors are both very expensive and difficult to obtain. In addition, the solubility of copper alkoxides is very low in organic solvents and yttrium alkoxides are readily hydrolysed even by a trace of water. Despite these difficulties, superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  has been prepared using alkoxides [157, 179–181]. A simple reaction involving  $\text{Y}(\text{OCHMe}_2)_3$ ,  $\text{Ba}(\text{OCHMe}_2)_2$  and  $\text{Cu}(\text{NBu}_2)_2$  in THF in an argon atmosphere gives the organometallic precursor [157]. The precursor powder, after removal of the solvent, is sintered at 973 K in flowing argon to obtain tetragonal  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . Following oxygenation at 673 K, the product shows a  $T_c$  of 85 K. Superconducting properties have been improved by using *n*-butoxides of Y, Ba and Cu in butanol solvent [179].

Alternatively, methoxyethoxides of yttrium, barium and copper have been used as precursors in methoxyethanol-methylethylketone-toluene solvent mixture to prepare  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  [180]. In some of the preparations,  $\text{Cu}(\text{NO}_3)_2$  (soluble in ethanol) or copper

acetylacetonate (soluble in toluene) is used along with the alkoxides of yttrium and barium to overcome the problem of low solubility of copper alkoxides [182, 183]. Organometallic precursors involving propionates [153] and neodeconates [184] have also been used for preparing  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ .

Modified sol-gel methods which do not involve the metal alkoxide precursors have been employed by many workers. Thus, Nagano and Greenblatt [185] have employed metal nitrates dissolved in ethylene glycol. After refluxing around 353 K under vigorous stirring, a bluish green colloidal gel is obtained. The gel is converted into orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  by heating to 1223 K in flowing oxygen. Precipitating all the three ions as hydroxides also results in fine colloidal particles of the starting materials [186–188]. The precipitation is generally carried out by the addition of  $\text{NH}_4\text{OH}$  [186],  $\text{N}(\text{CH}_3)_4\text{OH}$  [187] or  $\text{Ba}(\text{OH})_2$  [188] to a solution of metal nitrates (pH range 7–8). These hydroxides are decomposed around 1223 K in oxygen to give  $\text{YBa}_2\text{Cu}_3\text{O}_7$  showing a  $T_c$  of 93 K.

$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  has been prepared by the citrate gel process [189–193]. In this method 1 g equivalent of citric acid is added to each gram equivalent of the metal. The pH of the solution is adjusted to around 6 (either by  $\text{NH}_4\text{OH}$  or by ethylenediamine). Evaporation of the solvent (water) around 353 K, results in a viscous dark blue gel. The gel is decomposed and the powder sintered in the form of pellets at 1173 K in oxygen to obtain orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  ( $T_c = 93$  K). By this method, ultrafine homogeneous powders (particle size  $\sim 0.3 \mu\text{m}$ ) are obtained. The crucial step in this process is the adjustment of the pH which controls the stoichiometry of the final product. This limitation has been overcome by dispersing the citrate metal ion complexes in a solvent mixture of ethylene glycol and water [194, 195].

Problems such as the formation of  $\text{BaCO}_3$  during the calcination step, filtration and contamination of alkali metal ions in the final product are avoided in the sol-gel process. Furthermore, perfect homogeneity is obtained before calcination. The sol-gel process (e.g. citrate process) has the advantage over the other methods in that the gel can be used for making thick and thin superconducting films, fibres etc which have technological importance [179, 185, 186, 196–198].

#### 4.3. $\text{YBa}_2\text{Cu}_4\text{O}_8$

The sol-gel method offers a good alternative to the ceramic method for the synthesis of superconducting  $\text{YBa}_2\text{Cu}_4\text{O}_8$ . The following procedure has been used to prepare  $\text{YBa}_2\text{Cu}_4\text{O}_8$  at 1 atm oxygen pressure [199]. Appropriate quantities of  $\text{Y}(\text{n-OC}_4\text{H}_9)_3$ ,  $\text{Ba}(\text{s-OC}_4\text{H}_9)_2$  and  $\text{Cu}(\text{s-OBu})_2$  in butanol-xylene mixture are refluxed in an argon atmosphere at 343 K for a period of 30 h. The fine powder after the vigorous reaction is freed from the solvent and dried. The powder is heated in the form of pellets at 1033 K in flowing oxygen to obtain superconducting  $\text{YBa}_2\text{Cu}_4\text{O}_8$ .



used as the source of copper in this process [200].

In the modified citrate gel process to prepare  $\text{YBa}_2\text{Cu}_3\text{O}_x$  [201, 202], 1 g equivalent of citric acid is added for each gram equivalent of the metal and the pH of the solution is adjusted to  $\sim 5.5$  by the addition of ethylenediamine. The resulting clear solution is evaporated to yield a viscous purple gel. The decomposed gel is sintered in flowing oxygen for 3–5 days at 1088 K to obtain nearly monophasic  $\text{YBa}_2\text{Cu}_3\text{O}_x$  ( $T_c = 66$  K). Kakihana *et al* [203] have reported the preparation of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  using a precursor obtained from citrate metal ion complexes uniformly dispersed in a solvent mixture of ethylene glycol and water. This method yields phase-pure  $\text{YBa}_2\text{Cu}_3\text{O}_x$  ( $T_c \sim 79$  K) and eliminates the need to adjust the pH.

#### 4.4. Bismuth cuprates

There have been very few reports of the preparation of bismuth-based cuprate superconductors by the alkoxy sol-gel method [204]. Some of the difficulties arise because the relevant bismuth/lead alkoxides are not readily available; it is also not easy to get a common organic solvent to dissolve the various metal alkoxides simultaneously. Dhalle *et al* [204] have, however, attempted to synthesize the lead-doped  $n = 3$  member (2223) using organometallic precursors involving propionates. The starting materials were taken in the form of nitrates and converted into propionates by the addition of an excess of 100% propyl alcohol. This step was followed by the addition of ammonium hydroxide and ethylene glycol to increase the alkoxy anion concentration, thus in turn increasing the viscosity of the solution. All the solutions were mixed together and dried at 353 K. The resin after calcination at 1123 K in air and sintering at 1118 K gave a mixture of the  $n = 3$  and  $n = 2$  members.

A simple sol-gel method involving the addition of dilute ammonia to an aqueous solution containing nitrates of Bi, Sr and acetates of Ca, Cu and Pb (until the pH of the solution reached around 5.5) has also been employed to prepare bismuth cuprates [205, 206]. The blue solution after concentrating at around 343 K gives a viscous gel. The gel is decomposed and the powder sintered at around 1128 K in air. The product from this procedure is multiphasic showing a  $T_c$  of 104 K. The simplicity of the method and the formation of the  $n = 3$  phase in a short time makes it somewhat superior to the conventional ceramic route. The modified citrate gel process has been employed to prepare the  $n = 2$  member (2212) in pure form with a  $T_c$  of 78 K [193].

#### 4.5. Lead cuprates

The modified citrate gel process has been successfully employed by Mahesh *et al* [207] for the synthesis of lead cuprates of the 2213 or 1212 type. In a typical procedure, a mixture of citric acid and ethylene glycol in

is concentrated at 373 K to get a viscous gel. The gel after decomposition is heated in the form of pellets in the temperature range of 1073–1173 K either in  $\text{N}_2$  containing 1%  $\text{O}_2$  or in an oxygen atmosphere.  $\text{Pb}_2\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_{8+x}$  obtained from this process shows a sharp superconducting transition at 70 K. The 1212 cuprate also shows a sharp transition at 60 K. This process is superior to the ceramic procedure for synthesizing superconducting lead cuprates.

#### 5. Alkali flux method

Strong alkaline media, either in the form of solid carbonate fluxes, molten hydroxides or highly concentrated alkali solutions can be employed for the synthesis of high- $T_c$  cuprate superconductors. The alkali flux method takes advantage of both the moderate temperatures of the molten media (453–673 K) as well as of the acid-base characteristics of molten hydroxides to simultaneously precipitate oxides or oxide precursors such as hydroxides or peroxides of the constituent metals. The method stabilizes higher oxidation states of the metal by providing an oxidizing atmosphere.

Employing fused alkali hydroxides, Ham *et al* [208] have synthesized superconducting  $\text{La}_{2-x}\text{M}_x\text{CuO}_4$  ( $\text{M} = \text{K}$  or  $\text{Na}$  or vacancy) at relatively low temperatures (470–570 K). In this method, stoichiometric quantities of  $\text{La}_2\text{O}_3$  and  $\text{CuO}$  are added to a molten mixture containing  $\text{KOH}$  and  $\text{NaOH}$  (in an approximately 1:1 ratio) in a Teflon crucible and heated at around 570 K in air for 100 h. The 1:1 mixture of  $\text{KOH}$  and  $\text{NaOH}$  melts at 440 K and since the alkali hydroxides generally contain some water, the melt is acidic and can readily dissolve oxides such as  $\text{La}_2\text{O}_3$  and  $\text{CuO}$ . The black crystals obtained from the reaction (after washing away the excess hydroxide with water) show a  $T_c$  of 35 K. Since the reaction is carried out in alkali hydroxides, incorporation of  $\text{Na}^+$  or  $\text{K}^+$  ions for  $\text{La}^{3+}$  in the lattice of  $\text{La}_2\text{CuO}_4$  cannot be ruled out. It should be noted that superconducting alkali-doped  $\text{La}_2\text{CuO}_4$  is normally prepared at higher temperatures in sealed gold tubes [209]. Recently, alkaline hypobromite oxidation has been employed to obtain  $\text{La}_2\text{CuO}_{4+x}$  with a  $T_c$  of 44 K [210].

Superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_7$  ( $T_c \sim 88$  K) has also been prepared using the fused eutectic of sodium and potassium hydroxides in a similar manner to that described above [211]. The problem of contamination of alkali metals in the preparation of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  has been overcome by using the  $\text{Ba}(\text{OH})_2$  flux [211]. The procedure involves heating a mixture containing stoichiometric amounts of  $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ba}(\text{OH})_2$  and  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in an open ceramic crucible at around 1023 K in air for a short time (about 10 min) and then slowly cooling the melt to room temperature. Since  $\text{Ba}(\text{OH})_2$  has two hydration states, one melting at 351 K and the other at 681 K, the lower-melting hydrate acts as the solvent for the nitrates of copper



and yttrium while the high-melting hydrate serves as the medium for intimate mixing of the reactants. The precipitate obtained from the melt, after washing with water, is sintered in air at around 1173 K followed by oxygenation at 773 K. This method yields an orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_7$  phase (with little  $\text{CuO}$  impurity) showing a  $T_c$  of 92 K.

The flux method eliminates the need for mechanical grinding and introduction of carbon-containing anions, which is often encountered in the solution routes. Furthermore, the method is efficient and cost-effective.

## 6. Combustion method

Although many of the solution routes discussed earlier yield homogeneous products, the processes involved are quite complex. Combustion synthesis or self-propagating high-temperature synthesis (SHS), first developed by Merzhanov and Borovinskaya [212], provides a simple and rapid means of preparing inorganic materials, many of which are technologically important. Combustion synthesis is based on the principle that the heat energy liberated by many exothermic non-catalytic solid-solid or solid-gas reactions can self-propagate throughout the sample at a certain rate. This process can therefore occur in a narrow zone which separates the starting substances and reaction products.

Self-propagating combustion has been employed recently in this laboratory to synthesize members of almost all families of cuprate superconductors (except for the thallium cuprates) [213]. The method involves the addition of an appropriate fuel to a solution containing the metal nitrates in the proper stoichiometry. The ratio of the metal nitrates to the fuel is such that when the solution is dried at around 423 K, the solid residue undergoes flash combustion, giving an ash containing the mixture of oxides in the form of very fine particles (particle size 0.3–0.5  $\mu\text{m}$ ). The ash is then given proper heat treatment under the desired atmosphere to obtain the cuprate. The small particle size of the ash facilitates the reaction between the metal oxides due to smaller diffusion distances between the cations. Fuels such as urea [213, 214], glycine [213, 215] and tetraformal triazine (TFTA) [216] are generally employed for synthesizing cuprate superconductors. Ultrafine particles of copper metal can also act as an internal fuel wherein the combustion is initiated by flashing a laser beam for a short time [217]. Some of the cuprate superconductors which have been prepared [213] by this route include  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  ( $T_c = 35$  K),  $\text{YBa}_2\text{Cu}_3\text{O}_7$  ( $T_c = 90$  K),  $\text{YBa}_2\text{Cu}_4\text{O}_8$  ( $T_c = 80$  K),  $\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$  ( $T_c = 85$  K),  $\text{Pb}_2\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_8$  ( $T_c = 60$  K) and  $\text{Nd}_{1-x}\text{Ce}_x\text{CuO}_4$  ( $T_c \sim 30$  K).

## 7. Other methods

In addition to the various synthetic methods discussed hitherto, a few other methods such as spray drying [218–221], freeze drying [186, 222, 223], use of metallic precursors [224, 225] and electrochemical methods

[226, 227] have also been employed for the preparation of cuprate superconductors in bulk form. In spray drying, a solution containing the metallic constituents, usually in the form of nitrates, is sprayed in the form of fine droplets into a hot chamber. The solvent evaporates instantaneously, leaving behind an intimate mixture of the reactants which on heating at the desired temperature in a suitable atmosphere yields the cuprate. Some of the superconducting cuprates prepared by this method include  $\text{YBa}_2\text{Cu}_3\text{O}_7$  ( $T_c = 91$  K) [218],  $\text{YBa}_2\text{Cu}_4\text{O}_8$  ( $T_c = 81$  K) [219] and  $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$  ( $T_c = 101$  K) [220, 221]. In freeze drying, the reactants (in a common solvent) are frozen by immersing in liquid nitrogen. The solvent is removed at low pressures to obtain the initial reactants in fine powder form, and these are then processed at an appropriate temperature. For example,  $\text{YBa}_2\text{Cu}_3\text{O}_7$  ( $T_c = 87$  K) [186],  $\text{YBa}_2\text{Cu}_4\text{O}_8$  ( $T_c = 79$  K) [222] and  $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_{1.6}\text{Ca}_2\text{Cu}_3\text{O}_7$  ( $T_c = 101$  K) [223] have been prepared by this method.

Metallic precursors have been used in the preparation of 123 and 247 cuprates [224, 225]. For example, oxidizing an Er–Ba–Cu alloy around 1170 K gives superconducting  $\text{ErBa}_2\text{Cu}_3\text{O}_7$  with a  $T_c$  of 87 K [224]. Similarly  $\text{Yb}_2\text{Ba}_4\text{Cu}_8\text{O}_{13}$  has been obtained by heating an alloy composition of  $\text{YbBa}_2\text{Cu}_3$  (with 33 wt% of silver) under 1 atm oxygen at 1173 K [225].

Making use of electrochemical oxidation,  $\text{La}_2\text{CuO}_{4+x}$  with a  $T_c$  of 44 K has been prepared at room temperature, which is otherwise possible only by use of high oxygen pressures [226, 227].

## 8. Oxygen non-stoichiometry

Oxygen stoichiometry plays a crucial role in determining the superconducting properties of many of the cuprates. Thus, stoichiometric  $\text{La}_2\text{CuO}_4$  is an insulator, while an oxygen-excess material prepared under high oxygen pressures shows superconductivity with a  $T_c$  of 35 K [15]. The same holds for the next member of the homologous family,  $\text{La}_{2-x}\text{Sr}_x\text{CaCu}_2\text{O}_6$  which is superconducting only when there is an oxygen excess [17]. The excess oxygen donates holes in these two systems. In the case of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , oxygen can be easily removed giving rise to tetragonal non-superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_6$ . The  $\text{YBa}_2\text{Cu}_3\text{O}_6$  material can be prepared by heating  $\text{YBa}_2\text{Cu}_3\text{O}_7$  in an argon atmosphere at 973 K for extended periods of time [228]. The variation of  $T_c$  with oxygen stoichiometry,  $\delta$ , is well known [229, 230]. When  $\delta$  reaches 0.5, there is an intergrowth of  $\text{YBa}_2\text{Cu}_3\text{O}_6$  and  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , and at this composition, the material shows a  $T_c$  of 45 K. The  $\delta = 0.5$  composition is obtained by quenching  $\delta \approx 0$  material, heated in a nitrogen atmosphere at 743 K [231]. Similarly, by quenching  $\text{YBa}_2\text{Cu}_3\text{O}_7$  at 783 K in air,  $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}$  (showing a  $T_c$  of  $\sim 60$  K) is prepared [231]. The  $T_c$  of 90 K is found only when  $\delta \leq 0.2$ .  $\text{YBa}_2\text{Cu}_3\text{O}_6$  is readily oxidized back to  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . It may be noted that this oxidation–reduction process in

Cuprate	$T_c$ (approx.)	Methods of synthesis*
$\text{La}_{2-x}\text{Sr}_x(\text{Ba})\text{CuO}_4$	35	Ceramic*, sol-gel, combustion, coprecipitation
$\text{La}_2\text{Ca}_{1-x}\text{Sr}_x\text{Cu}_2\text{O}_8$	60	Ceramic (high $\text{O}_2$ pressure)*
$\text{La}_2\text{CuO}_{4+\delta}$	40	Ceramic (high $\text{O}_2$ pressure)* alkali-flux, hypobromite*
$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$	90	Ceramic (annealing in $\text{O}_2$ )*, sol-gel*, coprecipitation*, combustion
$\text{YBa}_2\text{Cu}_4\text{O}_8$	80	Ceramic (high $\text{O}_2$ pressure), ceramic (with $\text{Na}_2\text{O}_2$ )* sol-gel*, coprecipitation*
$\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$	90	Ceramic (air-quench)* sol-gel*, combustion, melt (glass) route*
$\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_2\text{O}_{10}$	110	Ceramic*, sol-gel, melt route
$\text{TlCaBa}_2\text{Cu}_2\text{O}_{8+\delta}$	90	Ceramic (sealed Ag/Au tube)*
$\text{TlCa}_2\text{Ba}_2\text{Cu}_2\text{O}_{8+\delta}$	115	Ceramic (sealed Ag/Au tube)*
$\text{Tl}_2\text{Ba}_2\text{CuO}_8$	90	Ceramic (sealed Ag/Au tube)*
$\text{Tl}_2\text{CaBa}_2\text{Cu}_2\text{O}_8$	110	Ceramic (sealed Ag/Au tube)*
$\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_2\text{O}_{10}$	125	Ceramic (sealed Ag/Au tube)*
$\text{Tl}_{0.5}\text{Pb}_{0.5}\text{CaSr}_2\text{Cu}_2\text{O}_{8+\delta}$	90	Ceramic (sealed Ag/Au tube)*
$\text{Pb}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_3\text{O}_8$	70	Ceramic (low $\text{O}_2$ partial pressure)*, sol-gel* (low $\text{O}_2$ partial pressure)
$\text{Pb}_{0.6}\text{Cu}_{0.6}\text{Sr}_2\text{Y}_{0.5}\text{Ca}_{0.6}\text{Cu}_2\text{O}_7$	45	Ceramic (flowing $\text{O}_2$ )*
$\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$	30	Ceramic (low $\text{O}_2$ partial pressure)*
		Coprecipitation (low $\text{O}_2$ partial pressure)*
$\text{Ca}_{1-x}\text{Sr}_x\text{CuO}_2$	40–110	Ceramic (high pressures)*
$\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$	40–110	Ceramic (high pressures)*

\* Recommended methods are indicated by asterisks.

\* Other rare-earth compounds of this type are also prepared by similar methods. Oxygen annealing is done below the orthorhombic-tetragonal transition.

\* Sr analogues of these compounds with different substitutions at Ca and Tl sites are prepared by a similar procedure.

$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  is of topochemical character. The other analogous rare-earth 123 cuprates also behave in a similar way with respect to the variation of  $\delta$  with  $T_c$  [237].

While  $\text{YBa}_2\text{Cu}_4\text{O}_8$  has high oxygen stability,  $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{13-\delta}$  shows a wide range of oxygen stoichiometry ( $0 \leq \delta \leq 1$ ) [233]. The maximum  $T_c$  of 90 K is achieved when  $\delta$  is close to zero, and when  $\delta$  reaches unity the material shows a  $T_c$  of 30 K; there is no structural phase transition accompanying the variation in oxygen stoichiometry. Usually, both yttrium 124 and 247 cuprates and their rare-earth analogues, prepared by the ceramic method under 1 atm oxygen pressure, show  $\delta$  close to zero.

Bismuth cuprates of the type  $\text{Bi}_2(\text{Ca}, \text{Sr})_{1-x}\text{Cu}_x\text{O}_{8+\delta}$  are best prepared by quenching the samples in air or by annealing in a nitrogen atmosphere at appropriate temperatures [53, 234]. Heating the samples in an oxygen atmosphere is no good, possibly because the extra oxygen may add on to the Bi-O layers. In the case of the lead-doped  $n = 3$  member (2223), preparing the samples under low partial pressures of oxygen is found to increase the volume fraction of the superconducting phase [235, 236]. The  $n = 1$  member,  $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+\delta}$ , shows metallic behaviour when there is excess oxygen [237]. By annealing in a reducing atmosphere (Ar or  $\text{N}_2$ ), the excess oxygen can be removed to induce superconductivity.

Oxygen stoichiometry has a dramatic influence on the superconducting properties of thallium cuprates [94, 108, 109, 238–246]. For example, thallium cuprates of the  $\text{TlCa}_{1-x}\text{Ba}_x\text{Cu}_2\text{O}_{8+\delta}$  family, derivatives of the

$\text{TlCa}_{1-x}\text{Sr}_x\text{Cu}_2\text{O}_{8+\delta}$  family and  $\text{Tl}_2\text{Ba}_2\text{CuO}_8$  often have excess oxygen when prepared in sealed tubes. By annealing these samples in a reducing atmosphere (Ar, dilute  $\text{H}_2$ ,  $\text{N}_2$  or vacuum) at appropriate temperatures, the excess oxygen is removed to induce superconductivity in some cases [108, 109, 238]. Annealing at low oxygen partial pressures or in a reducing atmosphere also increases the  $T_c$  of some of the superconducting thallium cuprates to higher values by decreasing the oxygen content [94, 239–246]. These variations are clearly related to the hole concentration where the number of holes decreases by removing excess oxygen, thereby giving the optimal concentration required for maximal  $T_c$  [247].

In lead cuprates of the  $\text{Pb}_2\text{Sr}_2(\text{La}, \text{Ca})\text{Cu}_3\text{O}_{8+\delta}$  (2213) type, increasing the oxygen content of the material by annealing in an oxygen atmosphere oxidizes the  $\text{Pb}^{2+}$  and  $\text{Cu}^{1+}$  without affecting the  $\text{CuO}_2$  sheets, which governs the superconductivity in this material [248]. Though this system shows a wide range of oxygen stoichiometry (associated with a structural phase transition from orthorhombic to tetragonal symmetry), maximum  $T_c$  is observed for any given composition where  $\delta$  is close to zero [249]. Samples with  $\delta \approx 0$  are therefore prepared by annealing in a nitrogen atmosphere containing little oxygen. The lead 1212 cuprates, on the other hand, are best prepared in a flowing oxygen atmosphere. The samples obtained after the oxygen treatment are often not superconducting since there is an oxygen excess. The samples are quenched in air at around 1073 K in order to achieve superconductivity [250].

Superconducting properties of the electron-doped superconductors,  $\text{Nd}_{1-x}\text{Ce}_x\text{CuO}_{4-x}$ , are sensitive to the oxygen content. The as-prepared samples which are semiconducting have oxygen content greater than four. Samples with oxygen content less than four are obtained by annealing in a reducing atmosphere ( $\text{N}_2$ , Ar or dilute  $\text{H}_2$ ) at around 1173 K. Maintaining the oxygen stoichiometry at less than four is essential for having an oxidation state of Cu less than 2+ in this material [25].

### 9. Concluding remarks

In the earlier sections we presented details of the preparative methods for the synthesis of various families of cuprate superconductors. In addition, we also examined the advantages and disadvantages of the different methods. Since more than one method of synthesis has been employed for preparing any given cuprate, it becomes necessary to make the right choice of method in any given situation. In order to assist in making such a choice, we have tabulated in table 6 the important preparative methods employed to synthesize some of the representative cuprates, where the recommended methods are also indicated.

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THE UNITED STATES OF AMERICA  
DOCTOR OF MEDICINE  
JAMES EARL RAY  
FUGITIVE  
WANTED  
\$50,000  
REWARD  
FOR ARREST  
AND RETURN  
TO THE UNITED STATES  
OF AMERICA  
OR  
\$10,000  
REWARD  
FOR INFORMATION  
LEADING TO HIS  
ARREST  
AND RETURN  
TO THE UNITED STATES  
OF AMERICA  
ALL INFORMATION  
SHOULD BE  
FURNISHED TO  
THE FBI  
AT WASHINGTON, D.C.  
20535  
OR TO THE  
LOCAL FBI OFFICE  
IN YOUR AREA  
FOR INFORMATION  
LEADING TO HIS  
ARREST  
AND RETURN  
TO THE UNITED STATES  
OF AMERICA  
A REWARD  
WILL BE PAID  
TO ANYONE  
WHO PROVIDES  
INFORMATION  
LEADING TO HIS  
ARREST  
AND RETURN  
TO THE UNITED STATES  
OF AMERICA  
IF THE INFORMATION  
IS DETERMINED  
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FEDERAL BUREAU  
OF INVESTIGATION  
OF THE  
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PERSONS ARE  
WANTED  
FOR ARREST  
AND RETURN  
TO THE UNITED STATES  
OF AMERICA  
JAMES EARL RAY  
FUGITIVE  
WANTED  
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REWARD  
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TO THE UNITED STATES  
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# **BRIEF ATTACHMENT AC**



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Serial No.: 08/479,810

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Group Art Unit: 1751

Examiner: M. Kopec

Commissioner for Patents  
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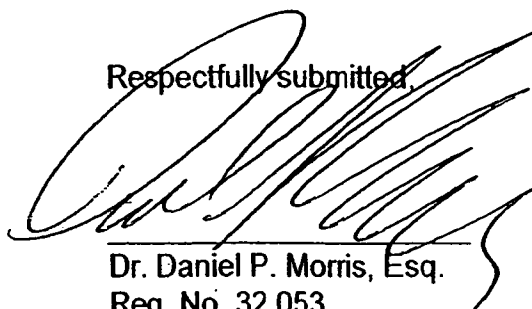
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**ATTACHMENT AC**



## HIGH TEMPERATURE

C. N. R. Rao and A. K. Raychaudhuri

The following tables give properties of a number of high temperature [redacted] Table 1 lists the crystal structure (space group and lattice constants) and the critical transition temperature  $T_c$  for the more important high temperature [redacted] so far studied. Table 2 gives energy gap, critical current density, and penetration depth in the superconducting state. Table 3 gives electrical and thermal properties of some of these materials in the normal state. The tables were prepared in November 1992 and updated in November 1994.

### REFERENCES

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# HIGH TEMPERATURE SUPERCONDUCTORS

C. N. R. Rao and A. K. Raychaudhuri

The following tables give properties of a number of high temperature superconductors. Table 1 lists the crystal structure (space group and lattice constants) and the critical transition temperature  $T_c$  for the more important high temperature superconductors so far studied. Table 2 gives energy gap, critical current density, and penetration depth in the superconducting state. Table 3 gives electrical and thermal properties of some of these materials in the normal state. The tables were prepared in November 1992 and updated in November 1994.

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**Table 1**  
**Structural Parameters and Approximate  $T_c$  Values of High-Temperature Superconductors**

Material	Structure	$T_c$ /K (maximum value)
$\text{La}_2\text{CuO}_{4+\delta}$	Bmab; $a = 5.355$ , $b = 5.401$ , $c = 13.15$ Å	39
$\text{La}_{2-x}\text{Sr}_x(\text{Ba}_y\text{CuO}_4)$	I4/mmm; $a = 3.779$ , $c = 13.23$ Å	35
$\text{La}_2\text{Ca}_{1-x}\text{Sr}_x\text{Cu}_2\text{O}_6$	I4/mmm; $a = 3.825$ , $c = 19.42$ Å	60
$\text{YBa}_2\text{Cu}_3\text{O}_7$	Pmmm; $a = 3.821$ , $b = 3.885$ , $c = 11.676$ Å	93
$\text{YBa}_2\text{Cu}_4\text{O}_8$	Ammm; $a = 3.84$ , $b = 3.87$ , $c = 27.24$ Å	80
$\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{15}$	Ammm; $a = 3.851$ , $b = 3.869$ , $c = 50.29$ Å	93
$\text{Bi}_2\text{Sr}_2\text{CuO}_6$	Amaa; $a = 5.362$ , $b = 5.374$ , $c = 24.622$ Å	10
$\text{Bi}_2\text{CaSr}_2\text{Cu}_2\text{O}_8$	$A_2aa$ ; $a = 5.409$ , $b = 5.420$ , $c = 30.93$ Å	92
$\text{Bi}_2\text{Ca}_2\text{Sr}_2\text{Cu}_3\text{O}_{10}$	$A_2aa$ ; $a = 5.39$ , $b = 5.40$ , $c = 37$ Å	110
$\text{Bi}_2\text{Sr}_2(\text{Ln}_{1-x}\text{Ce}_x)_2\text{Cu}_2\text{O}_{10}$	P4/mmm; $a = 3.888$ , $c = 17.28$ Å	25
$\text{Ti}_2\text{Ba}_2\text{CuO}_6$	$A_2aa$ ; $a = 5.468$ , $b = 5.472$ , $c = 23.238$ Å; I4/mmm; $a = 3.866$ , $c = 23.239$ Å	92
$\text{Ti}_2\text{CaBa}_2\text{Cu}_2\text{O}_8$	I4/mmm; $a = 3.855$ , $c = 29.318$ Å	119
$\text{Ti}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$	I4/mmm; $a = 3.85$ , $c = 35.9$ Å	128
$\text{Ti}(\text{BaLa})\text{CuO}_5$	P4/mmm; $a = 3.83$ , $c = 9.55$ Å	40
$\text{Ti}(\text{SrLa})\text{CuO}_5$	P4/mmm; $a = 3.7$ , $c = 9$ Å	40
$(\text{Ti}_{0.5}\text{Pb}_{0.5})\text{Sr}_2\text{CuO}_5$	P4/mmm; $a = 3.738$ , $c = 9.01$ Å	40
$\text{TiCaBa}_2\text{Cu}_2\text{O}_7$	P4/mmm; $a = 3.856$ , $c = 12.754$ Å	103
$(\text{Ti}_{0.5}\text{Pb}_{0.5})\text{CaSr}_2\text{Cu}_2\text{O}_7$	P4/mmm; $a = 3.80$ , $c = 12.05$ Å	90
$\text{TiSr}_2\text{Y}_{0.5}\text{Ca}_{0.5}\text{Cu}_2\text{O}_7$	P4/mmm; $a = 3.80$ , $c = 12.10$ Å	90
$\text{TiCa}_2\text{Ba}_2\text{Cu}_3\text{O}_8$	P4/mmm; $a = 3.853$ , $c = 15.913$ Å	110
$(\text{Ti}_{0.5}\text{Pb}_{0.5})\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_9$	P4/mmm; $a = 3.81$ , $c = 15.23$ Å	120
$\text{TiBa}_2(\text{La}_{1-x}\text{Ce}_x)_2\text{Cu}_2\text{O}_9$	I4/mmm; $a = 3.8$ , $c = 29.5$ Å	40
$\text{Pb}_2\text{Sr}_2\text{La}_{0.5}\text{Ca}_{0.5}\text{Cu}_3\text{O}_8$	Cmmm; $a = 5.435$ , $b = 5.463$ , $c = 15.817$ Å	70
$\text{Pb}_2(\text{SrLa})_2\text{Cu}_2\text{O}_6$	P22 <sub>1</sub> 2; $a = 5.333$ , $b = 5.421$ , $c = 12.609$ Å	32
$(\text{Pb,Cu})\text{Sr}_2(\text{La,Ca})\text{Cu}_2\text{O}_7$	P4/mmm; $a = 3.820$ , $c = 11.826$ Å	50
$(\text{Pb,Cu})(\text{Sr,Eu})(\text{Eu,Ce})\text{Cu}_2\text{O}_x$	I4/mmm; $a = 3.837$ , $c = 29.01$ Å	25
$\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$	I4/mmm; $a = 3.95$ , $c = 12.07$ Å	30
$\text{Ca}_{1-x}\text{Sr}_x\text{CuO}_2$	P4/mmm; $a = 3.902$ , $c = 3.35$ Å	110
$\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$	P4/mmm; $a = 3.942$ , $c = 3.393$ Å	40
$\text{Ba}_{0.6}\text{K}_{0.4}\text{BiO}_3$	Pm3m; $a = 4.287$ Å	31
$\text{Rb}_2\text{CsC}_{60}$	$a = 14.493$ Å	31
$\text{NdBa}_2\text{Cu}_3\text{O}_7$	Pmmm; $a = 3.878$ , $b = 3.913$ , $c = 11.753$	58

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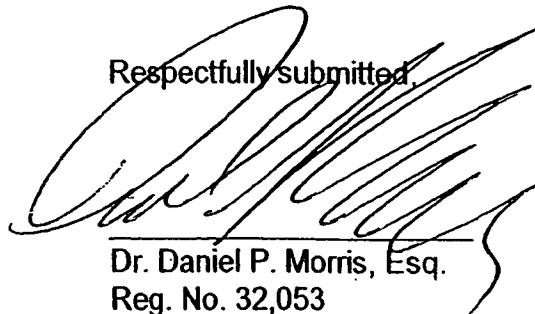
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**ATTACHMENT AD**

# THEORY OF SUPERCONDUCTIVITY

By

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## CHAPTER 1

### Fundamental Facts

(a) Superconductivity was discovered in 1911 by Kamerlingh-Onnes.<sup>1</sup> He was the first to liquefy helium and so to produce temperatures below 10° K. With this new technique he was able to observe the continued decrease of the electrical resistance of metals with decreasing temperature. With mercury, in contrast to other metals, he was astonished to find that the resistance completely vanished, almost discontinuously, at about 4.2° K (Fig. 1-1). Today superconductivity is known in 18 other metals (see Table 1-1) whereas in others, e. g., gold and bismuth, the conductivity remains normal far below even 1° K. Many alloys and compounds can also become superconducting, in particular the frequently used niobium nitride which has a transition temperature as high as 20° K. However, among these latter substances hysteresis phenomena mentioned in the "Introduction" are so much more strongly evident that in testing the present theory we prefer to employ only the "good" superconductors, i. e., the pure elements.

In the ideal case the resistance vanishes completely and discontinuously at a transition temperature  $T_c$ . Actually the resistance-temperature curve does fall more sharply the more the specimen is like a single crystal and the smaller the measuring current used. Because the drop always occurs in a measurable temperature range, the experimental definition of the transition temperature is to some extent arbitrary. The temperature at which the direct-current resistance reaches one half of the value it had just before the drop is generally given as the transition temperature, because this can be measured accurately. However, a high-frequency investigation to be described in Chap. 16 (f) indicates that the foot of the curve where

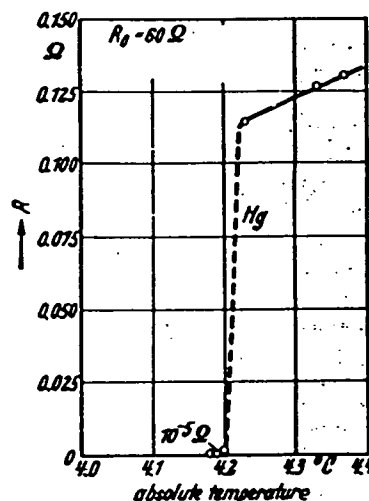


Fig. 1-1. Appearance of superconductivity in mercury according to H. Kamerlingh-Onnes (1911). The ordinate is the resistance  $R$ ;  $R_0$ , the resistance of solid mercury extrapolated to 0° C, is 60 ohms.

<sup>1</sup>H. Kamerlingh-Onnes, *Commun. Leiden*, 120b, 122b, 124c, (1911).

# **BRIEF ATTACHMENT AE**



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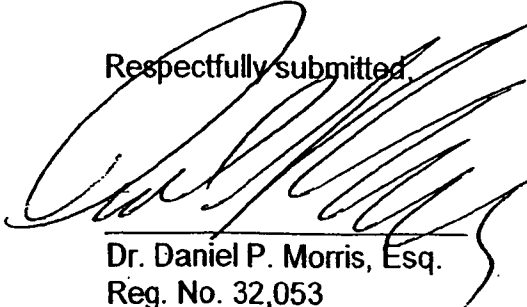
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# EUROPEAN PATENT APPLICATION

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(54) **New superconductive compounds of the K<sub>2</sub>NiF<sub>4</sub> structural type having a high transition temperature, and method for fabricating same.**

(57) The superconductive compounds are oxides of the general formula  $RE_{2-x}AE_xTM.O_{4-y}$ , wherein RE is a rare earth, AE is a member of the group of alkaline earths or a combination of at least two member of that group, and TM is a transition metal, and wherein  $x < 0.3$  and  $0.1 \leq y \leq 0.5$ . The method for making these compounds involves the steps of coprecipitating aqueous solutions of the respective nitrates of the constituents and adding the coprecipitate to oxalic acid, decomposing the precipitate and causing a solid-state reaction at a temperature between 500 and 1200°C for between one and eight hours, forming pellets of the powdered product at high pressure, sintering the pellets at a temperature between 500 and 1000°C for between one half and three hours, and subjecting the pellets to an additional annealing treatment at a temperature between 500 and 1200°C for between one half and five hours in a protected atmosphere permitting the adjustment of the oxygen content of the final product.

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# NEW SUPERCONDUCTIVE COMPOUNDS OF THE KNIFE STRUCTURAL TYPE HAVING A HIGH TRANSITION TEMPERATURE, AND METHOD FOR FABRICATING SAME

## Field of the Invention

The invention relates to a new class of superconductors, in particular to components of the  $K_2NiF_4$  type of structure having superconductor properties below a relatively high transition temperature, and to a method for manufacturing those compounds.

## Background of the Invention

Superconductivity is usually defined as the complete loss of electrical resistance of a material at a well-defined temperature. It is known to occur in many materials: About a quarter of the elements and over 1000 alloys and components have been found to be superconductors. Superconductivity is considered a property of the metallic state of the material, in that all known superconductors are metallic under the conditions that cause them to superconduct. A few normally non-metallic materials, for example, become superconductive under very high pressure, the pressure converting them to metals before they become superconductors.

Superconductors are very attractive for the generation and energy-saving transport of electrical power over long distances, as materials for forming the coils of strong magnets for use in plasma and nuclear physics, in nuclear resonance medical diagnosis, and in connection with the magnetic levitation of fast trains. Power generation by thermonuclear fusion, for example, will require very large magnetic fields which can only be provided by superconducting magnets. Certainly, superconductors will also find application in computers and high-speed signal processing and data communication.

While the advantages of superconductors are quite obvious, the common disadvantage of all superconductive materials so far known lies in their very low transition temperature (usually called the critical temperature  $T_c$ ) which is typically on the order of a few degrees Kelvin. The element with the highest  $T_c$  is niobium (9.2 K), and the highest known  $T_c$  is about 23 K for  $Nb_3Ge$  at ambient pressure.

Accordingly, most known superconductors require liquid helium for cooling and this, in turn, requires an elaborate technology and as a matter of principle involves a considerable investment in cost and energy.

It is, therefore, an object of the present inven-

tion to propose compositions for high- $T_c$  superconductors and a manufacturing method for producing compounds which exhibit such a high critical temperature that cooling with liquid helium is obviated so as to considerably reduce the cost involved and to save energy.

The present invention proposes to use compounds having a layer-type structure of the kind known from potassium nickel fluoride  $K_2NiF_4$ . This structure is in particular present in oxides of the general composition  $RE_2TM.O_4$ , wherein RE stands for the rare earths (lanthanides) and TM stands for the so-called transition metals. It is a characteristic of the present invention that in the compounds in question the RE portion is partially substituted by one member of the alkaline earth group of metals, or by a combination of the members of this alkaline earth group, and that the oxygen content is at a deficit.

For example, one such compound that meets the description given above is lanthanum copper oxide  $La_2CuO_4$  in which the lanthanum -which belongs to the IIIB group of elements- is in part substituted by one member of the neighboring IIA group of elements, viz. by one of the alkaline earth metals (or by a combination of the members of the IIA group), e.g., by barium. Also, the oxygen content of the compound is incomplete such that the compound will have the general composition  $La_{2-x}Ba_xCuO_{4-y}$ , wherein  $x \leq 0.3$  and  $y < 0.5$ .

Another example for a compound meeting the general formula given above is lanthanum nickel oxide wherein the lanthanum is partially substituted by strontium, yielding the general formula  $La_{2-x}Sr_xNiO_{4-y}$ . Still another example is cerium nickel oxide wherein the cerium is partially substituted by calcium, resulting in  $Ce_{2-x}Ca_xNiO_{4-y}$ .

The following description will mainly refer to barium as a partial replacement for the lanthanum in a  $La_2CuO_4$  compound because it is the Ba-La-Cu-O system which is, at least at present, the best understood system of all possible. Some compounds of the Ba-La-Cu-O system have been described by C. Michel and B. Raveau in Rev. Chim. Min. 21 (1984) 407, and by C. Michel, L. Er-Rakho and B. Raveau in Mat. Res. Bull., Vol. 20, (1985) 667-671. They did, however, not find nor try to find, superconductivity.

Experiments conducted in connection with the present invention have revealed that high- $T_c$  superconductivity is present in compounds where the rare earth is partially replaced by any one or more of the other members of the same IIA group of elements, i.e. the other alkaline earth metals. Ac-

tually, the  $T_c$  of  $\text{La}_2\text{CuO}_{4-y}$  with  $\text{Sr}^{2+}$  is higher and is superconductivity-induced diamagnetism larger than that found with  $\text{Ba}^{2+}$  and  $\text{Ca}^{2+}$ .

As a matter of fact, only a small number of oxides is known to exhibit superconductivity, among them the Li-Ti-O system with onsets of superconductivity as high as 13.7 K, as reported by D.C. Johnston, H. Prakash, W.H. Zachariasen and R. Visvanathan in *Mat. Res. Bull.* 8 (1973) 777. Other known superconductive oxides include Nb-doped  $\text{SrTiO}_3$  and  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ , reported respectively by A. Baratoff and G. Binnig in *Physics* 108B (1981) 1335, and by A.W. Sleight, J.L. Gillson and F.E. Bierstedt in *Solid State Commun.* 17 (1975) 27.

The X-ray analysis conducted by Johnston et al. revealed the presence in their Li-Ti-O system of three different crystallographic phases, one of them, with a spinel structure, showing the high critical temperature. The Ba-La-Cu-O system, too, exhibits a number of crystallographic phases, namely with mixed-valent copper constituents which have itinerant electronic states between non-Jahn-Teller  $\text{Cu}^{3+}$  and Jahn-Teller  $\text{Cu}^{2+}$  ions.

This applies likewise to systems where nickel is used in place of copper, with  $\text{Ni}^{3+}$  being the Jahn-Teller constituent, and  $\text{Ni}^{2+}$  being the non-Jahn-Teller constituent.

The existence of Jahn-Teller polarons is conducting crystals was postulated theoretically by K.H. Hoeck, H. Nickisch and H. Thomas in *Helv. Phys. Acta* 56 (1983) 237. Polarons have large electron-phonon interactions and, therefore, are favorable to the occurrence of superconductivity at high critical temperatures.

Generally, the Ba-La-Cu-O system, when subjected to X-ray analysis reveals three individual crystallographic phases, viz.

- a first layer-type perovskite-like phase, related to the  $\text{K}_2\text{NiF}_4$  structure, with the general composition  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$ , with  $x \ll 1$  and  $y \approx 0$ ;
- a second, non-conducting CuO phase; and
- a third, nearly cubic perovskite phase of the general composition  $\text{La}_{1-x}\text{Ba}_x\text{CuO}_{3-y}$ , which appears to be independent of the exact starting composition,

as has been reported in the paper by J.G. Bednorz and K.A. Müller in *Z. Phys. B - Condensed Matter* 64 (1988) 189-193. Of these three phases the first one appears to be responsible for the high- $T_c$  superconductivity, the critical temperature showing a dependence on the barium concentration in that phase. Obviously, the  $\text{Ba}^{2+}$  substitution causes a mixed-valent state of  $\text{Cu}^{2+}$  and  $\text{Cu}^{3+}$  to preserve charge neutrality. It is assumed that the oxygen deficiency,  $y$ , is the same in the doped and undoped crystallites.

Both  $\text{La}_2\text{CuO}_4$  and  $\text{LaCuO}_3$  are metallic conduc-

tors at high temperatures in the absence of barium. Actually, both are metals like  $\text{LaNiO}_3$ . Despite their metallic character, the Ba-La-Cu-O type materials are ceramics, as are the other compounds of the  $\text{RE}_2\text{TM}_2\text{O}_4$  type, and their manufacture more or less follows the known principles of ceramic fabrication. The preparation of a Ba-La-Cu-O compound, for example, in accordance with the present invention typically involves the following manufacturing steps:

- Preparing aqueous solutions of the respective nitrates of barium, lanthanum and copper and coprecipitation thereof in their appropriate ratios.
- Adding the coprecipitate to oxalic acid and forming an intimate mixture of the respective oxalates.
- Decomposing the precipitate and causing a solid-state reaction by heating the precipitate to a temperature between 500 and 1200°C for one to eight hours.

- Pressing the resulting product at a pressure of about 4 kbar to form pellets.

- Re-heating the pellets to a temperature between 500 and 900°C for one half to three hours for sintering.

It will be evident to those skilled in the art that if the partial substitution of the lanthanum by strontium or calcium is desired, the particular nitrate thereof will have to be used in place of the barium nitrate of the example described above. Also, if the copper of this example is to be replaced by another transition metal, the nitrate thereof will obviously have to be employed.

Experiments have shown that the partial contents of the individual compounds in the starting composition play an important role in the formation of the phases present in the final product. While, as mentioned above, the final Ba-La-Cu-O system obtained generally contains the said three phases, with the second phase being present only to a very small amount, the partial substitution of lanthanum by strontium or calcium (and perhaps beryllium) will result in only one phase existing in the final  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$  or  $\text{La}_{2-x}\text{Ca}_x\text{CuO}_{4-y}$ , respectively, provided  $x < 0.3$ .

With a ratio of 1:1 for the respective (Ba, La) and Cu contents, one may expect the said three phases to occur in the final product. Setting aside the said second phase, i.e. the CuO phase, whose amount is negligible, the relative volume amounts of the other two phases are dependent on the barium contents in the  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$  complex. At the 1:1 ratio and with an  $x \approx 0.02$ , the onset of a localization transition is observed, i.e., the resistivity increases with decreasing temperature, and there is no superconductivity.

With  $x = 0.1$  at the same 1:1 ratio, there is a resistivity drop at the very high critical temperature of 35 K.

With a (Ba,La) versus Cu ratio of 2:1 in the starting composition, the composition of the  $\text{La}_2\text{CuO}_4\text{:Ba}$  phase, which was assumed to be responsible for the superconductivity, is imitated, with the result that now only two phases are present, the CuO phase not existing. With a barium content of  $x = 0.15$ , the resistivity drop occurs at  $T_c = 26$  K.

The method for preparing the Ba-La-Cu-O complex involves two heat treatments for the precipitate at an elevated temperature for several hours. In the experiments carried out in connection with the present invention it was found that best results were obtained at  $900^\circ\text{C}$  for a decomposition and reaction period of 5 hours, and again at  $900^\circ\text{C}$  for a sintering period of one hour. These values apply to a ratio 1:1 composition as well as to a 2:1 composition.

For the ratio 2:1 composition, a somewhat higher temperature is permissible owing to the melting point of the composition being higher in the absence of excess copper oxide. Yet it is not possible by high-temperature treatment to obtain a one-phase compound.

Measurements of the dc conductivity were conducted between 300 and 4.2 K. For barium-doped samples, for example, with  $x < 0.3$ , at current densities of  $0.5 \text{ A/cm}^2$ , a high-temperature metallic behavior with an increase in resistivity at low temperatures was found. At still lower temperatures, a sharp drop in resistivity ( $>90\%$ ) occurred which for higher current densities became partially suppressed. This characteristic drop was studied as a function of the annealing conditions, i.e. temperature and oxygen partial pressure. For samples annealed in air, the transition from itinerant to localized behavior was not found to be very pronounced, annealing in a slightly reducing atmosphere, however, led to an increase in resistivity and a more pronounced localization effect. At the same time, the onset of the resistivity drop was shifted towards higher values of the critical temperature. Longer annealing times, however, completely destroy the superconductivity.

Cooling the samples from room temperature, the resistivity data first show a metal-like decrease. At low temperatures, a change to an increase occurs in the case of Ca compounds and for the Ba-substituted samples. This increase is followed by a resistivity drop, showing the onset of superconductivity at  $22 \pm 2$  K and  $33 \pm 2$  K for the Ca and Ba compounds, respectively. In the Sr compound, the resistivity remains metallic down to the resistivity drop at  $40 \pm 1$  K. The presence of localization effects, however, depends strongly on alkaline-earth ion concentration and sample preparation, that is to say, annealing conditions and also on the density which have to be optimized. All samples with low

concentrations of Ca, Sr, and Ba show a strong tendency to localization before the resistivity drop occur.

Apparently, the onset of the superconductivity, i.e. the value of the critical temperature  $T_c$ , is dependent, among other parameters, on the oxygen content of the final compound. It seems that a certain oxygen deficiency is necessary for the material to have a high- $T_c$  behavior. In accordance with the present invention, the method described above for making the  $\text{La}_2\text{CuO}_4\text{:Ba}$  complex is complemented by an annealing step during which the oxygen content of the final product can be adjusted. Of course, what was said in connection with the formation of the  $\text{La}_2\text{CuO}_4\text{:Ba}$  compound, likewise applies to other compounds of the general formula  $\text{RE}_2\text{TM}_x\text{O}_4\text{:AE}$ , such as, e.g.  $\text{Nd}_2\text{NiO}_4\text{:Sr}$ .

In the cases where a heat treatment for decomposition and reaction and/or for sintering was performed at a relatively low temperature, i.e. at no more than  $950^\circ\text{C}$ , the final product is subjected to an annealing step at about  $900^\circ\text{C}$  for about one hour in a reducing atmosphere. It is assumed that the net effect of this annealing step is a removal of oxygen atoms from certain locations in the matrix of the  $\text{RE}_2\text{TM}_x\text{O}_4$  complex, thus creating a distortion in its crystalline structure. The  $\text{O}_2$  partial pressure for annealing in this case may be between  $10^1$  and  $10^5$  bar.

In those cases where a relatively high temperature (i.e. above  $950^\circ\text{C}$ ) was employed for the heat treatment, it might be advantageous to perform the annealing step in a slightly oxidizing atmosphere. This would make up for an assumed exaggerated removal of oxygen atoms from the system owing to the high temperature and resulting in a too severe distortion of the system's crystalline structure.

Resistivity and susceptibility measurements, as a function of temperature, of  $\text{Sr}^{2+}$  and  $\text{Ca}^{2+}$ -doped  $\text{La}_2\text{CuO}_{4-y}$  ceramics show the same general tendency as the Ba<sup>2+</sup>-doped samples: A drop in resistivity  $\rho(T)$ , and a crossover to diamagnetism at a slightly lower temperature. The samples containing  $\text{Sr}^{2+}$  actually yielded a higher onset than those containing Ba<sup>2+</sup> and Ca<sup>2+</sup>. Furthermore, the diamagnetic susceptibility is about three times as large as for the Ba samples. As the ionic radius of  $\text{Sr}^{2+}$  nearly matches the one of  $\text{La}^{3+}$ , it seems that the size effect does not cause the occurrence of superconductivity. On the contrary, it is rather adverse, as the data on Ba<sup>2+</sup> and Ca<sup>2+</sup> indicate.

The highest  $T_c$ 's for each of the dopant ions investigated occur for those concentrations where, at room temperature, the  $\text{Re}_{2-x}\text{TM}_x\text{O}_{4-y}$  structure is close to the orthorhombic-tetragonal structural phase transition which may be related to the substantial electron-phonon interaction enhanced by the substitution. The alkaline-earth substitution of

the rare earth metal is clearly important, and quite likely creates TM ions with no  $e_g$  Jahn-Teller orbitals. Therefore, the absence of these J.-T. orbitals, that is, J.-T. holes near the Fermi energy probably plays an important role for the  $T_c$  enhancement.

## Claims

1) Superconductive compound of the  $RE_2TM.O_4$  type having a transition temperature above 20 K, wherein the rare earth (RE) is partially substituted by one or more members of the alkaline earth groups of elements (AE), and wherein the oxygen content is adjusted such that the resulting crystal structure is distorted and comprises a phase of the general composition  $RE_{2-x}AE_xTM.O_{4-y}$ , wherein TM represents a transition metal, and  $x < 0.3$  and  $y < 0.5$ .

2) Compound in accordance with claim 1, wherein the rare earth (RE) is lanthanum and the transition metal (TM) is copper.

3) Compound in accordance with claim 1, wherein the rare earth is cerium and the transition metal is nickel.

4) Compound in accordance with claim 1, wherein the rare earth is lanthanum and the transition metal is nickel.

5) Compound in accordance with claim 1, wherein barium is used as a partial substitute for the rare earth, with  $x < 0.3$  and  $0.1 \leq y \leq 0.5$ .

6) Compound in accordance with claim 1, wherein calcium is used as a partial substitute for the rare earth, with  $x < 0.3$  and  $0.1 \leq y \leq 0.5$ .

7) Compound in accordance with claim 1, wherein strontium is used as a partial substitute for the rare earth, with  $x < 0.3$  and  $0.1 \leq y \leq 0.5$ .

8) Compound in accordance with claim 1, wherein the rare earth is lanthanum and the transition metal is chromium.

9) Compound in accordance with claim 1, wherein the rare earth is neodymium and the transition metal is copper.

10) Method for making superconductive compounds of the  $RE_2TM.O_4$  type, with RE being a rare earth, TM being a transition metal, the compounds having a transition temperature above 20 K, comprising the steps of:

- preparing aqueous solutions of the nitrates of the rare earth and transition metal constituents and of one or more of the alkaline earth metals and coprecipitation thereof in their appropriate ratios;
- adding the coprecipitate to oxalic acid and forming an intimate mixture of the respective oxalates;
- decomposing the precipitate and causing a solid-state reaction by heating the precipitate to a temperature between 500 and 1200°C for a period of

time between one and eight hours;

- allowing the resultant powder product to cool;
- pressing the powder at a pressure of between 2 and 10 kbar to form pellets;

5 - re-adjusting the temperature of the pellets to a value between 500 and 1000°C for a period of time between one half and three hours for sintering;

- subjecting the pellets to an additional annealing treatment at a temperature between 500 and 1200°C for a period of time between one half and 5 hours in a protected atmosphere permitting the adjustment of the oxygen content of the final product which has a final composition of the form  $RE_{2-x}TM.O_{4-y}$ , wherein  $x < 0.3$  and  $0.1 < y < 0.5$ .

11) Method in accordance with claim 10, wherein the protected atmosphere is pure oxygen.

12) Method in accordance with claim 10, wherein the protected atmosphere is a reducing atmosphere with an oxygen partial pressure between  $10^{-1}$  and  $10^{-5}$  bar.

13) Method in accordance with claim 10, wherein the decomposition step is performed at a temperature of 900°C for 5 hours, and wherein the annealing step is performed at a temperature of 900°C for one hour in a reducing atmosphere with an oxygen partial pressure between  $10^{-1}$  and  $10^{-5}$  bar.

14) Method in accordance with claim 10, wherein lanthanum is used as the rare earth and copper is used as the transition metal, and wherein barium is used to partially substitute for the lanthanum, with  $x < 0.2$ , wherein the decomposition step is performed at a temperature of 900°C for 5 hours, and wherein the annealing step is performed in a reducing atmosphere with an oxygen partial pressure on the order of  $10^{-3}$  bar and at a temperature of 900°C for one hour.

15) Method in accordance with claim 10, wherein lanthanum is used as the rare earth and nickel is used as the transition metal, and wherein barium is used to partially substitute for the lanthanum, with  $x < 0.2$ , wherein the decomposition step is performed at a temperature of 900°C for 5 hours, and wherein the annealing step is performed in a reducing atmosphere with an oxygen partial pressure on the order of  $10^{-3}$  bar and at a temperature of 900°C for one hour.

16) Method in accordance with claim 10, wherein lanthanum is used as the rare earth and copper is used as the transition metal, and wherein calcium is used to partially substitute for the lanthanum, with  $x < 0.2$ , wherein the decomposition step is performed at a temperature of 900°C for 5 hours, and wherein the annealing step is performed in a reducing atmosphere with an oxygen partial pressure on the order of  $10^{-3}$  bar and at a temperature of 900°C for one hour.

17) Method in accordance with claim 10, wherein lanthanum is used as the rare earth and copper is used as the transition metal, and wherein strontium is used to partially substitute for the lanthanum, with  $x < 0.2$ , wherein the decomposition step is performed at a temperature of  $900^{\circ}\text{C}$  for 5 hours, and wherein the annealing step is performed in a reducing atmosphere with an oxygen partial pressure on the order of  $10^{-3}$  bar and at a temperature of  $900^{\circ}\text{C}$  for one hour.

18) Method in accordance with claim 10, wherein cerium is used as the rare earth and nickel is used as the transition metal, and wherein barium is used to partially substitute for the cerium, with  $x < 0.2$ , wherein the decomposition step is performed at a temperature of  $900^{\circ}\text{C}$  for 5 hours, and wherein the annealing step is performed in a reducing atmosphere with an oxygen partial pressure on the order of  $10^{-3}$  bar and at a temperature of  $900^{\circ}\text{C}$  for one hour.

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# **BRIEF ATTACHMENT AF**



**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of

Applicants: Bednorz et al.

Serial No.: 08/479,810

Filed: June 7, 1995

For: **NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION**

Date: March 14, 2005

Docket: YO987-074BZ

Group Art Unit: 1751

Examiner: M. Kopec

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

**THIRD SUPPLEMENTAL AMENDMENT**

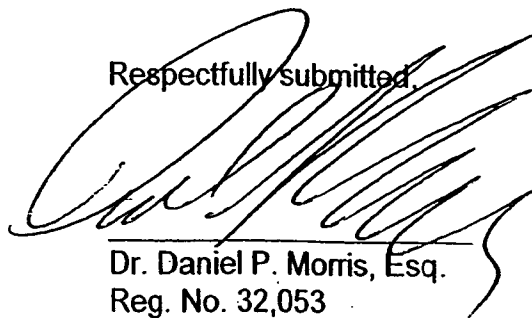
Sir:

In response to the Office Action dated July 28, 2004, please consider the following:

The attachments referred to herein A to Z and AA are in the **FIRST SUPPLEMENTAL AMENDMENT**. The Attachments AB to AG are attached herein.

Please charge any fee necessary to enter this paper and any previous paper to deposit account 09-0468.

Respectfully submitted,



Dr. Daniel P. Morris, Esq.  
Reg. No. 32,053  
(914) 945-3217

IBM CORPORATION  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, New York 10598

**ATTACHMENT AF**

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# COPPER OXIDE SUPERCONDUCTORS

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**Timir Datta**  
**Horacio A. Farach**

*with help from*

**M. M. Rigney**  
**C. R. Sanders**

*Department of Physics and Astronomy  
University of South Carolina  
Columbia, South Carolina*



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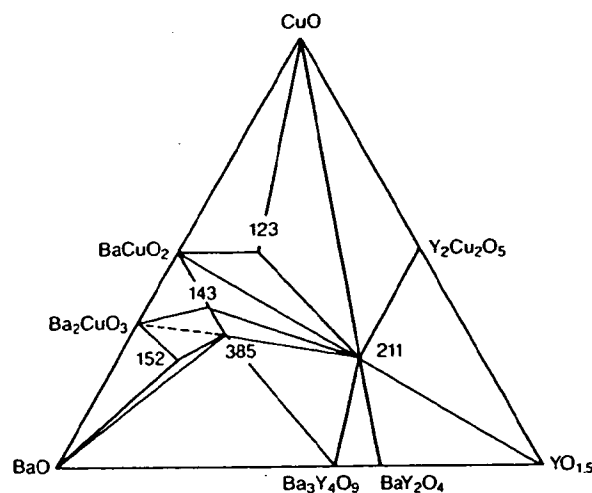
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Printed in the United States of America

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Compound	Slowly cooled to room temperature
123 - $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+\delta}$	$\text{O}_7$
143 - $\text{YBa}_4\text{Cu}_3\text{O}_{8.5+\delta}$	$\text{O}_9$
385 - $\text{Y}_3\text{Ba}_8\text{Cu}_5\text{O}_{17.5+\delta}$	$\text{O}_{18}$
152 - $\text{YBa}_5\text{Cu}_2\text{O}_{8.5+\delta}$	$\text{O}_9$
211 - $\text{Y}_2\text{BaCuO}_5$	
$\text{Ba}_2\text{CuO}_{3+\delta}$	$\text{O}_{33}$

Fig. V-2. Ternary phase diagram of the  $\text{Y}_2\text{O}_3$ -BaO-CuO system at  $950^\circ\text{C}$ . The green phase [ $\text{Y}_2\text{BaCuO}_5$ , (211)] the superconducting phase [ $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , (123)], and three other compounds are shown in the interior of the diagram (DeLee).

## B. METHODS OF PREPARATION

In this section three methods of preparation will be described, namely, the solid state, the coprecipitation, and the sol-gel techniques (Hatfi). The widely used solid-state technique permits off-the-shelf chemicals to be directly calcined into superconductors, and it requires little familiarity with the subtle physicochemical processes involved in the transformation of a mixture of compounds into a superconductor. The coprecipitation technique mixes the constituents on an atomic scale and forms fine powders, but it requires careful control of the pH and some familiarity with analytical chemistry. The sol-gel procedure requires more competence in analytical procedures.

In the solid-state reaction technique one starts with oxygen-rich compounds of the desired components such as oxides, nitrates, or carbonates of Ba, Bi, La, Sr, Tl, Y, or other elements. Sometimes nitrates are formed first by dissolving oxides in nitric acid and decomposing the solution at  $500^\circ\text{C}$  before calcination

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bulk supercon- h as thin films ys of checking or subsolidus Fig. V-2 con- l-point oxides  $^\circ$ , ( $\text{Ba}_3\text{CuO}_4$ ),  $7$ ), along the ig green phase n the interior urther, Kuzzz, ). Compounds workers. The so), and then

(e.g., Davis, Holla, Kelle). These compounds are mixed in the desired atomic ratios and ground to a fine powder to facilitate the calcination process. Then these room-temperature-stable salts are reacted by calcining for an extended period ( $\approx 20$  hr) at elevated temperatures ( $\approx 900^\circ\text{C}$ ). This process may be repeated several times, with pulverizing and mixing of the partially calcined material at each step. As the reaction proceeds, the color of the charge changes. The process usually ends with a final oxygen anneal followed by a slow cool down to room temperature of the powder, or pellets made from the powder, by sintering in a cold or hot press. Sintering is not essential for the chemical process, but for transport and other measurements it is convenient to have the material pelletized. A number of researchers have provided information on this solid-state reaction approach (e.g., Allge, Finez, Galla, Garla, Gopal, Gubse, Hajk1, Hatan, Herrm, Hikal, Hirab, Jayar, Maen1, Mood1, Mood2, Neume, Poepp, Polle, Qadri, Rhyne, Ruzic, Saito, Sait1, Sawa1, Shamo, Takit, Tothz, Wuzz3).

Some of the earlier works on foils, thick films, wires, or coatings employed a suspension of the calcined powder in a suitable organic binder, and the desired product was obtained by conventional industrial processes such as extruding, spraying, or coating.

In the second or coprecipitation process the starting materials for calcination are produced by precipitating them together from solution (e.g., Asela, Bedno, Leez7, Wang2). This has the advantage of mixing the constituents on an atomic scale. In addition the precipitates may form fine powders whose uniformity can be controlled, which can eliminate some of the labor. Once the precipitate has been dried, calcining can begin as in the solid-state reaction procedure. A disadvantage of this method, at least as far as the average physicist or materials scientist is concerned, is that it requires considerable skill in chemical procedures.

Another procedure for obtaining the start-up powder is the sol-gel technique in which an aqueous solution containing the proper ratios of Ba, Cu, and Y nitrates is emulsified in an organic phase and the resulting droplets are gelled by the addition of a high-molecular-weight primary amine which extracts the nitric acid. This process was initially applied to the La materials, but has been perfected for YBaCuO as well (Cimaz, Hatfi).

When using commercial chemical supplies to facilitate the calcination process a dry or wet (acetone) pregrinding with an agate mortar and pestle or a ball mill is recommended. Gravimetric amounts of the powdered precursor materials are thoroughly mixed and placed in a platinum or ceramic crucible. Care must be taken to ensure the compatibility of the ceramic crucible with the chemicals to obviate reaction and corrosion problems.

Complete recipes for the YBa\* material have been described (e.g., Gran2). Typically, the mixture of unreacted oxides is calcined in air or oxygen around  $900^\circ\text{C}$  for 15 hr. During this time the YBaCuO mixture changes color from the green  $\text{Y}_2\text{BaCuO}_5$  phase to the dark gray  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  compound. Then the charge is taken out, crushed, and scanned with X rays to determine its purity. If warranted by the powder pattern X-ray scan, the calcination process is repeated. Often, at this stage the material is very oxygen poor, and electrically it is semi-

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conducting or even nonconducting. After pelletizing at  $>10^5$  psi the pellet is sintered for several hours at  $\approx 900^\circ\text{C}$  in flowing oxygen and then slowly cooled at  $\approx 3^\circ\text{C}/\text{min}$  down to room temperature. Slow cooling from the elevated temperature is important for producing the low-temperature orthorhombic superconductor phase. The tetragonal nonsuperconducting phase may be obtained by quenching. The pellet may be used as is or it may be cut into suitable sizes by sand blasting, with a diamond saw, or with an arc. After vigorous machining another oxygen anneal ( $450^\circ\text{C}$ , 1 hr, slow cool down) is often required to preserve the superconducting properties.

An example of preparing a Bi-based superconductor involves mixing gravimetric amounts of high-purity  $\text{Bi}_2\text{O}_3$ ,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ , and  $\text{CuO}$  powders, calcining them in air at  $750$ – $890^\circ\text{C}$ , regrounding them, and then repeating these procedures several times. Then pellets of the calcined product were sintered at the same temperature and quenched to room temperature (Chuz5). Figure V-1 shows the effect of sample treatment on the resistance versus temperature curve.

**WARNING:** As was mentioned above, thallium is a toxic material and proper precautions must be taken when working with it. It is useful to start by preparing the high-quality precursor compound  $\text{BaCu}_3\text{O}_4$  or  $\text{Ba}_2\text{Cu}_3\text{O}_5$  by reacting the oxides in air at  $925^\circ\text{C}$  for 24 hr. Then appropriate amounts of  $\text{Tl}_2\text{O}_3$  are added, powdered, and pelletized. The pellet is then heated to  $880$ – $910^\circ\text{C}$  for a few minutes in flowing oxygen, and at the onset of melting it is quenched to room temperature (Shen1).

Allen Hermann has suggested consulting the following references for information on thallium poisoning and antidotes thereto: H. Heydlauf, *Euro. J. Pharmacol.* 6, 340 (1969), which discusses thallium poisoning and describes the antidote ferric cyanoferrate, and *Int. J. Pharmacol.* 10, 1 (1974), which discusses cases of thallium intoxication treated with Prussian Blue.

### C. ADDITIONAL COMMENTS ON PREPARATION

This section will treat some additional methods which have been employed for the preparation of samples.

In one experiment coprecipitated nitrates of La, Sr, Cu, and Na carbonate were calcined for 2 hr at  $825^\circ\text{C}$ , pressed into pellets, and then subjected to shock compression of  $\approx 20$  GPa at an estimated peak temperature of  $\approx 1000^\circ\text{C}$  (Graha). The best superconductivity was observed after 1 hr of air exposure at  $1100^\circ\text{C}$ . Shock compression fabrication has also been reported (Murrz, Murr1) for  $\text{YBa}_*$  and other rare-earth derivatives. This process produced "monoliths," distinct from the usual composites.

Another technique involved the formation of a precursor alloy of Eu, Ba, Cu or Yb, Ba, Cu by rapid solidification, with the superconducting materials obtained subsequently by oxidation (Halda). A novel method involved preparing

the superconductors from molten Ba-Cu oxides and solid rare-earth-containing materials. In principle this process may be better controlled and complicated shapes can be molded or cast (Herma).

Pulsed current densities of  $300\text{--}400 \text{ Å/cm}^2$  with rise times of  $0.6 \text{ μsec}$  at room temperature were used to convert the weakly semiconducting phase of YBaCuO to the stable metallic phase (Djure, Djur1).

A claim was made that thermal cycling from cryogenic temperatures to  $240 \text{ K}$  raised the  $T_c$  of YBa\* and YBaCuO-F (with some F substituting for O) to  $159 \text{ K}$ . Cycling above  $140 \text{ K}$  lowered  $T_c$ . This cycling process could possibly change the density of twins and thereby enhance  $T_c$ .

A freeze-drying technique was reported as producing sintered materials homogeneous in composition and small in porosity (Stras). The low-temperature firing of oxalates ( $T < 780^\circ\text{C}$ ) has also been reported as producing a homogeneous material of small grain size (Manth).

Both Bi and Pb act as fluxes during the sintering process (Kilco). Bismuth substitution appears to reduce the normal state resistivity by about an order of magnitude without affecting the superconducting properties.

A convenient method of separating the superconducting particles from a powdered mixture using magnetic levitation has been reported (Barso). This may be used to select the superconducting fraction after each calcination process.

#### D. FILMS

The new ceramic oxide superconductors presently lack mechanical properties such as ductility which are needed for high-current applications like magnet wire fabrication (Jinzz-Jinz3) and power transmission. To circumvent some of these deficiencies for microelectronic applications one can prepare thin films on suitable substrates. Some devices such as Josephson junctions require thin superconducting films. Many workers have discussed the preparation and properties of LaSrCuO- (e.g., Adach, Delim, Kawas, Koinu, Matsu, Nagat, Naito, Tera1) and YBaCuO- (e.g., Burbi, Charz, Evett, Gurvi, Hause, Hongz, Inamz, Kwozz, Kwoz1, Manki, Scheu, Somek, Wuzz4) type films.

Almost every conceivable thin-film deposition technique such as electron beam evaporation, molecular beam epitaxy, sputtering, magnetron, laser ablation, screening, and spraying has been tried with the copper oxide system. Some of these techniques require expensive, elaborate apparatus, although descriptions of simple thin-film deposition systems are also available (e.g., see Koin1). Some representative examples of deposition procedures will be discussed.

Epitaxial films of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  on (100)  $\text{SrTiO}_3$  were produced using three separate electron beam sources (e.g., Chaud, Chau1, Laibo). The deposition was done in  $10^{-4}\text{--}10^{-3}$  torr  $\text{O}_2$  with a substrate temperature of  $400^\circ\text{C}$ . The deposited films were atomically amorphous with a broad X-ray peak. The epitaxial ordering was achieved upon annealing in  $\text{O}_2$  at  $900^\circ\text{C}$  with the orthorhombic  $c$  axis essentially perpendicular to the plane.

High-quality beam to evaporate torr (Hammo, Cited film in oxygen  $750^\circ\text{C}$  for 1 hr, furnace.

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Films of dysprosium beam epitaxy (process was monitored copper was incorporated amorphous Ba high-temperature

Films of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  thickness of  $500 \text{ Å}$  deposited on  $\text{SrTiO}_3$  pellet of YBaCuO. The evaporation rate  $6 \text{ Hz}$ ,  $\approx 30 \text{ nsec}$  heated to  $450^\circ\text{C}$  they appeared oxygen annealed hours. Standard superconductivity achieved LaSr\* (Moorj)

Films were and Cu in layers  $200^\circ\text{C}$  and  $10^{-7}$  layers to diffuse conducting composite conductivity with  $\text{Y}_2\text{O}_3$ , and Ba

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High-quality superconducting films were obtained using a multiple electron beam to evaporate metallic sources in a flow of molecular oxygen at  $4-5 \times 10^{-6}$  torr (Hammo, Ohzzz). The deposition rate was 10 Å/sec. To anneal the deposited film in oxygen it was heated for 3-6 hr in a flow of oxygen at 650°C, raised to 750°C for 1 hr, then to 850°C for 1 hr, and finally slowly cooled down in the furnace.

Superconducting films were prepared using a double ion beam sputtering arrangement (Madak). The target beam was Ar at 40 mA, and the substrate beam was Ar or an Ar-O<sub>2</sub> mixture at 10-500 eV and 2 mA. The base pressure was  $5 \times 10^{-7}$  torr and, with the gas,  $4 \times 10^{-4}$  torr. The best substrate materials such as ZrO<sub>2</sub>-9% Y<sub>2</sub>O<sub>3</sub> did not appreciably interact, diffuse, or change the deposited films. The films were  $\approx 1 \mu$ m thick and were rendered superconducting by oxygen annealing. Zero resistance was attained at 88 K. The superconducting properties depended upon the ion beam energy, substrate temperature, annealing conditions, composition, and the extent of poisoning from the substrate.

Films of dysprosium barium copper oxide were grown (Webbz) by molecular beam epitaxy (MBE) using a Varian 360 MBE system, and the nucleation process was monitored by reflection high-energy electron diffraction (RHEED). The copper was incompletely oxidized in metallic microcrystals growing in a sea of amorphous Ba and Dy. After deposition superconducting films were obtained by high-temperature oxygen annealing.

Films of Y<sub>1.1</sub>Ba<sub>1.5</sub>Cu<sub>3</sub>O<sub>6.4</sub> approximately 3300 Å thick with a surface roughness of 500 Å were prepared (Dijkk, Inamz, Wuzz4). These films were deposited on SrTiO<sub>3</sub>, sapphire, and vitron carbon by evaporation from a single bulk pellet of YBaCuO 1 cm diameter and 0.2 cm thick at a pressure of  $5 \times 10^{-7}$  torr. The evaporation was produced by several thousand pulses of laser irradiation (3-6 Hz,  $\approx 30$  nsec width, 1 J/pulse, 2 J/cm<sup>2</sup>). For best results the substrate was heated to 450°C. As deposited thin films were well bonded to the substrate and they appeared shiny dark brown and were electrically insulating. The films were oxygen annealed at 900°C for 1 hr and then slowly cooled over a period of several hours. Standard four-probe resistivity measurements indicated the onset of superconductivity around 95 K and, for a (100) SrTiO<sub>3</sub> substrate, with zero resistivity achieved near 85 K. The laser ablation technique was also employed for LaSr\* (Moorj) and YBa\* (Nara1).

Films were obtained from sandwiched multilayers by depositing Y<sub>2</sub>O<sub>3</sub>, BaO, and Cu in layers (Nasta, Tsaur) on ZrO<sub>2</sub>, MgO, and sapphire substrates at 200°C and  $10^{-5}$  torr. Oxygen treatment for 1-2 hr at  $\approx 850^\circ\text{C}$  permitted the layers to diffuse, homogenize, and oxygenate, and thereby form the superconducting compound (Baozz). Films on Ni have also been reported in which superconductivity was obtained by a diffusion process involving the Cu substrate, Y<sub>2</sub>O<sub>3</sub>, and BaCO<sub>3</sub> composite (Tachi).

Some 5000-Å thick films of YBaCuO have been deposited using an ultrahigh vacuum dc-magnetron getter-sputter deposition system. The deposition rate was 0.2 Å/sec, the substrate temperature was 1050°C, and the target-to-substrate distance was 12 cm. The scattering was done in an Ar-O<sub>2</sub> atmosphere.



The X-ray and electron microscope examinations indicated some variation among the substrates arranged on the heater. Inhomogeneities were observed even within the film made on a single substrate. As deposited the films were oxygen deficient, and annealing produced suitable compositions. The reversible oxygen incorporation was monitored by the systematic splitting of the strongest X-ray peaks. The oxygen diffusion coefficient at 600°C was  $10^{-15}$  m<sup>2</sup>/sec and the activation energies for desorption and absorption were 1.1 and 1.7 eV, respectively. The highest onset temperature was 99 K with complete superconduction at 40 K. Exposure to water inhibited the superconductor (Barns, Kishi, Yanzz). A device structure with a Y<sub>2</sub>O<sub>3</sub> barrier has also been studied (Blami).

Another work showed that films produced by dc magnetron sputtering are copper deficient if the substrate-to-target distance is large or if the substrate is at an elevated temperature (Leez5).

Superconducting YBaCuO thin films with a large surface area ( $\approx 5$  cm  $\times$  5 cm) were grown on Al<sub>2</sub>O<sub>3</sub>, sapphire, and MgO up to a 500°C substrate temperature by magnetron and diode techniques. Rutherford back scattering (RBS) indicated a uniform composition across magnetron-deposited film areas with diameters up to 5 cm, and the diode film composition homogeneity was even better, but over a smaller area ( $\approx 2.5$  cm diameter). The as-deposited films were annealed in oxygen at different temperatures and exposure times. Prolonged high-temperature annealing ( $> 850^\circ\text{C}$ ) increased the impurity phase. The highest  $T_c$  films had a wide range of composition, with the maximum  $T_c$  film copper rich. On the basis of an in-situ resistivity study of YBa\* thin films a rapid heating to about 900°C in flowing helium followed by slow cool down in flowing oxygen was recommended (David).

The post-deposition anneal cycle was avoided by producing the films in a high-pressure reactive evaporation process involving rapid thermal annealing (Lathr). Smooth films were obtained on zirconia and SrTiO<sub>3</sub> substrates. Screen printing of oxide superconducting films is also possible (Budha, Fuzz1), and simple spray deposition has been reported (Gupta). Films have also been made by coating and spinning off the solutions. Aqueous and aqueous-alcoholic mixed solutions of the metal nitrates (Coop2), metal acetates in dilute acetic acid (Rice1), and sol-gels (Kram1) have all been reported. These processes are potentially important for commercial superconducting coatings on silicon (Kram1), on yttrium-stabilized zirconia (YSZ), on SrTiO<sub>3</sub> (Coop2, Gupta), and on MgO (Gupta, Rice1).

## E. SINGLE CRYSTALS

The bulk properties of oxide superconductors are averages over components parallel and perpendicular to the Cu-O planes. In addition, for orthorhombic samples there is an averaging over properties that differ for the  $a$  and  $b$  directions in this plane. This in-plane anisotropy is especially pronounced for the YBa\* 123 structure in which the Cu-O-Cu-O chains lie along the  $b$  axis. The

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best way to understand these materials is through experiments on perfect single crystals. Unfortunately, untwinned  $\text{YBa*}$  crystals are not available so the  $a, b$  anisotropy cannot be resolved. Tetragonal superconductors should not have this twinning problem. In this work twinned monocrystals will be referred to as single crystals.

A number of experiments have been carried out on monocrystals such as X-ray diffraction (e.g., Borde, Hazen, Lepad, Siegr, Onoda), magnetic studies (e.g., Crabt, Schn1, Worth), mechanical measurements (e.g., Cookz, Dinger), and micro-Raman spectroscopy (e.g., Hemle). In this section we will briefly describe how such crystals are made. The December 1987 issue of the *Journal of Crystal Growth* was devoted to superconductors.

Millimeter-size  $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4$  single crystals were grown in a molten copper oxide flux (Kawa1). Another basic technique employs other fluxes (Haned, Taka4, Zhou1), namely,  $\text{PbF}_2$ ,  $\text{B}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{PbO}_2$ , with the risk of possible Pb contamination.  $\text{LaSr*}$  crystals were also grown by the solid phase reaction using a hot press of pellets (Iwazu) and rapid quenching of a nonstoichiometric melt (Satoz).

Small single crystals of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  have been prepared from a sintered powder which was formed into a pellet and then heated, first in a reducing atmosphere and then in an oxidizing one at  $925^\circ\text{C}$ . Annealing a stoichiometric mixture also produced monocrystals (Liuzz). Millimeter-size crystals were grown by melting a stoichiometric mixture of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  plus excess  $\text{CuO}$  at  $1150^\circ\text{C}$  followed by holding at  $900^\circ\text{C}$  for 4 days (Damen, see also Fine1).

A gold crucible on a gold or alumina sheet was used to obtain free-standing ( $1 \times 2 \times 0.1 \text{ mm}$ ) single crystals of  $\text{YBa*}$  (Kaise, Kais1, Holtz). A charge of 2 g was heated in air at  $200^\circ\text{C}/\text{hr}$  and held at  $975^\circ\text{C}$  for 1.5 hr, then it was cooled to  $400^\circ\text{C}$  at  $25^\circ\text{C}/\text{hr}$ . The molten charge creeps and forms single crystals and twins on the surfaces. The larger crystals formed in the space between the bottom of the crucible and the gold support sheet.

A detailed account has appeared of the preparation of a 123 compound single crystal by the flux method (Zhou1). The flux mole ratio  $\text{BaO}_2:\text{CuO}$  was between 1:3 and 2:5, and the nutrient  $\text{Y}_2\text{O}_3:\text{BaO}_2:\text{CuO}$  mole ratios were 0.5:2:3. A multistep temperature process was employed. Black single crystals of  $\text{YBa*}$  were found at the bottom and at the edge between the wall and the bottom of the crucibles. Platinum crucibles seemed to contaminate the samples so alumina crucibles were recommended. Crystals as large as  $2 \times 2 \times 0.3 \text{ mm}^3$  were reported. A similar technique was used to produce single crystals of  $\text{YBa*}$  and  $\text{DyBa*}$  as large as 4 mm (Schn1).

## F. ALIGNED GRAINS

Clearly high-quality single crystals are important for understanding the physics of superconductors. However, much useful information about anisotropies can

be obtained by studying the properties of aligned grains, which are much easier to fabricate.

A superconducting sample can be initially a collection of randomly oriented grains, but various techniques can be used to partially orient these grains so that the *c* axis lies preferentially in a particular direction. For example uniaxial compression tends to orient compacted grains, with compressed 90- $\mu\text{m}$  particles exhibiting more alignment than compressed 10- $\mu\text{m}$  particles (Glowa). Epoxy-embedded grains have been aligned under the influence of an applied magnetic field and pressure (Arend).

X-ray and magnetic measurements have been reported on aligned crystalline grains of YBa\* (Farr1). Optical studies have also been made on aligned grains. The critical current density for samples cut parallel to the compression axis of such grains was nearly isotropic with respect to the direction of an applied magnetic field, and it was a factor of 6 smaller than that for the samples cut perpendicular to this axis (Glowa).

## G. REACTIVITY

The oxide superconductors are not inert materials, but rather they are sensitive to exposure to certain gases and to surface contact with particular materials. Great care must be exercised to avoid contamination from water vapor and carbon dioxide in the atmosphere. In addition these materials are catalytic to oxygenation reactions, and these factors result in the occurrence of various chemical and other interactions, especially at elevated temperatures. The granular and porous nature of the materials has an accelerating effect on such reactions.

Samples of YBaCuO may degrade in a matter of days when exposed to an ordinary ambient atmosphere; they react readily with liquid water, acids, and electrolytes, and moderately with basic solutions. The reaction with water (Barns, Kishi, Yanzz) produces nonsuperconducting cuprates. The effects of acetone and other organics (McAnd) have been determined, and stable carboxyl groups have been found in the YBaCuO lattice (Parmi).

Hydrogen enters the YBaCuO lattice at elevated temperatures and forms a solid solution. Low concentrations have very little effect and high concentrations degrade the superconducting properties (Berni, Reill, Yang3). The effects of exposure to oxygen at elevated temperature and oxidation have been discussed several places in this review (e.g., Blend, Engle, Tara3).

The foregoing evidence for the reactivity of the oxide superconductors makes it necessary to consider methods of passivation or protecting them from long-term degradation. An epoxy coating was found to provide some protection (Barns). Coating the surface with metals can be deleterious since metals such as Fe (Gaoz1, Hillz, Weave) and Ti (Meyel) react with the surface of LaSrCuO or YBaCuO. There is evidence for the passivation of the surface of LaSr\* with gold (Meyer).

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## H. THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis (TGA) consists of monitoring the weight of a sample during a heating or cooling cycle. For example, one might determine the oxygen content of a superconducting material by measuring its weight change in an oxidizing ( $O_2$  or air) or reducing (e.g., 4%  $H_2$  in Ar) atmosphere. Typical procedures consist of heating or cooling at  $20^\circ C/min$ . The relative accuracy of the method is about 0.005 (Ongz1). Many workers (e.g., Beye3, Hauck, Huan1, John4, Leez7, Maruc, Ohish, Ongz1, Tara7, Zhuzz) are now using TGA or differential thermal analysis (DTA) routinely during their sample preparation procedures.

## I. CHECKS ON QUALITY

After a sample has been prepared it is necessary to check its quality as a superconductor. Most investigators employ the four-probe resistivity check to determine whether it superconducts, and at what temperature it transforms to the superconducting state. A sharp, high  $T_c$  transition is an indicator of a high-quality sample. Another widely used quality control method is the determination of the magnetic susceptibility of the specimen. Good quality is indicated by a sharp, high  $T_c$  transition with both the flux exclusion and flux expulsion close to  $-1/4\pi$ . This is, in a sense, a more fundamental check on quality since the value of the susceptibility far below the transition temperature is a good indicator of the fraction of the sample that is superconducting (see Section III-D).

In addition to its superconducting properties, it is also of interest to know the chemical composition and the structure of the specimen. The nominal composition is deduced from the relative proportions of the various cations in the starting material. Chemical analysis and some more sophisticated techniques such as XPS, electrospectroscopic chemical analysis (ESCA), and an electron microprobe that is favorable for low-atomic-weight elements are applicable here. Most investigators only report the cation concentrations in the specimen. Oxygen content is much more difficult to determine, but is important to know. Rutherford back-scattering experiments (John1, Wuzz1, Wuzz4) can provide oxygen contents, and metallography characterizes grain sizes.

The structures of the oxide superconductors described in Chapter VI are easily checked by the X-ray powder pattern method. Many articles list the lattice constants  $a$ ,  $b$ ,  $c$  of samples and mention whether they are tetragonal ( $a = b \neq c$ ) or orthorhombic ( $a \approx b \neq c$ ). Narrow lines and the absence of spurious signals indicate a good, single-phase sample. Typical X-ray diffraction powder patterns for  $LaSr^*$  (Skelt) and  $YBa^*$  presented in Figs. V-3 and V-4, respectively, may be used to compare with patterns obtained from freshly prepared samples.

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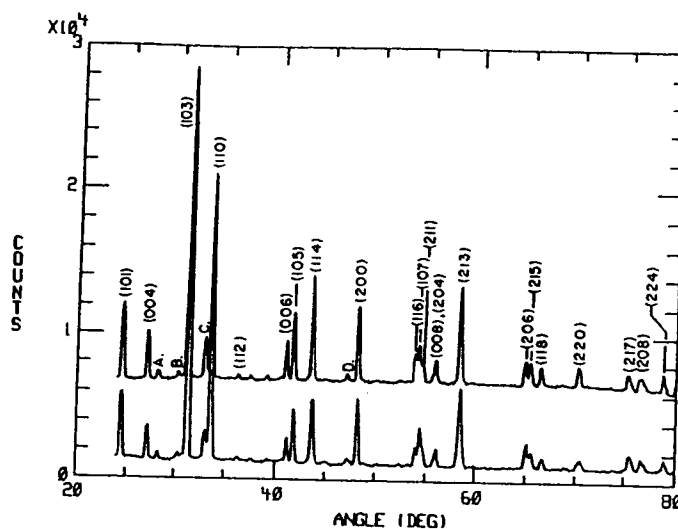


Fig. V-3. Room-temperature (upper curve) and 24-K (lower curve) X-ray diffraction powder patterns of  $(\text{La}_{0.925}\text{Ba}_{0.075})_2\text{CuO}_4$  (Skelt).

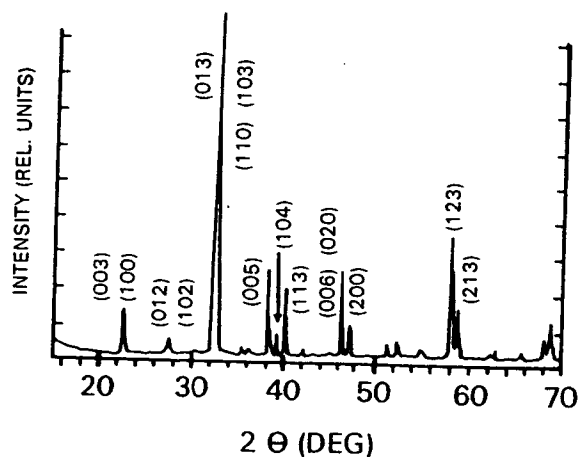


Fig. V-4. Room-temperature X-ray diffraction powder pattern of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . (Provided by C. Almasan, J. Estrada, and W. E. Sharp.)

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## J. RESISTIVITY MEASUREMENT

A measurement of the resistance  $R(T)$  or resistivity  $\rho(T)$  of a material versus the temperature is the principal technique employed to determine when a material becomes superconducting. The transition temperature manifests itself by a sharp drop in resistivity to zero. The simplest way to make this measurement is to apply a voltage across the sample and measure the current flow through it, but such a two-probe method (Baszy) is not very satisfactory, and is seldom used. Most resistivity determinations are made with the four-probe technique to be described below, although more sophisticated arrangements such as a six-probe method (Kirsch) can also be used. The fabrication of low-resistance contacts by silver glazing has been reported (Vand2). These researchers pointed out the importance of a low-contact resistance ( $\rho < 10 \mu\Omega/\text{mm}^2$  at 77 K) for making transport  $J_C$  measurements.

The specimen resistance as a function of temperature is generally determined in a suitable cryostat by attaching leads or electrodes to it in the standard four-probe configuration. Two leads or probes carry a known constant current  $I$  into and out of the specimen, and the other two leads measure the potential drop between two equipotential surfaces resulting from the current flow. For superconducting specimens the leads are often arranged in a linear configuration, with the contacts for the input current on the ends, and those for the measurement voltage near the center.

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# **BRIEF ATTACHMENT AG**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of

Applicants: Bednorz et al.

Serial No.: 08/479,810

Filed: June 7, 1995

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Date: March 14, 2005

Docket: YO987-074BZ

Group Art Unit: 1751

Examiner: M. Kopec

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

**THIRD SUPPLEMENTAL AMENDMENT**

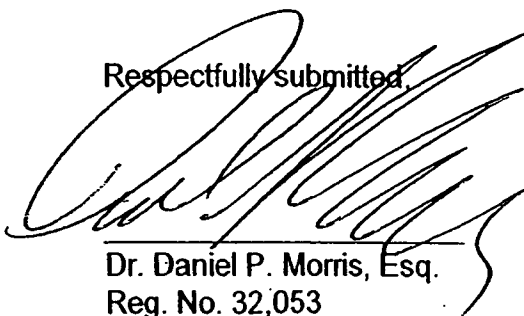
Sir:

In response to the Office Action dated July 28, 2004, please consider the  
following:

The attachments referred to herein A to Z and AA are in the FIRST  
SUPPLEMENTAL AMENDMENT. The Attachments AB to AG are attached herein.

Please charge any fee necessary to enter this paper and any previous paper to  
deposit account 09-0468.

Respectfully submitted,



Dr. Daniel P. Morris, Esq.  
Reg. No. 32,053  
(914) 945-3217

IBM CORPORATION  
Intellectual Property Law Dept.  
P.O. Box 218  
Yorktown Heights, New York 10598

**ATTACHMENT AG**



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# *The New Superconductors*

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Table 8.1. Progress in Raising the Superconducting Transition Temperature  $T_c$  Since the Discovery of Cuprates in 1986

Material	$T_c$ (K)	Year
$\text{Ba}_x\text{La}_{5-x}\text{Cu}_5\text{O}_9$	30–35	1986
$(\text{La}_{0.9}\text{Ba}_{0.1})_2\text{Cu}_4\text{O}_{4-x}$ (at 1-GPa pressure) <sup>a</sup>	52	1986
$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$	95	1987
$\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$	110	1988
$\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$	125	1988
$\text{Tl}_2\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (at 7-GPa pressure)	131	1993
$\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+x}$	133	1993
$\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ (at 30-GPa pressure)	147	1994

<sup>a</sup>A pressure of 1 GPa is about 10,000 atm.

While this increase in  $T_c$  itself is an amazing result, a high-transition temperature is not the only property required to make new compounds useful for applications. For example if materials are to be used as wires in magnets, they must be malleable and ductile rather than brittle; in addition they must have high critical currents in large magnetic fields. Critical currents as high as those in niobium-tin have not yet been achieved in forms of the new materials that can easily be made into wires, although there are reports of comparable values in thin films on various substrates.

The Holy Grail that is being sought is a transition temperature much above room temperature. We say much above because devices must operate significantly below the transition  $T_c$  so that the critical current  $J_c$  and critical magnetic field  $B_c$  are sufficiently high. Very close to the transition temperature, the critical magnetic field is usually quite small, but we see from Figs. 3.4 and 3.5 that  $B_c$  and  $J_c$  continuously increase as the temperature is lowered below  $T_c$ . We need an operating temperature far below the critical surface in Fig. 3.15 so that both  $B_c$  and  $J_c$  are sufficiently large for the desired application.

### 8.3. LAYERED STRUCTURE OF THE CUPRATES

All cuprate superconductors have the layered structure shown in Fig. 8.1: The flow of supercurrent takes place in conduction layers, and binding layers support and hold together the conduction layers. Conduction layers contain copper-oxide ( $\text{CuO}_2$ ) planes of the type shown in Fig. 8.2; each copper ion ( $\text{Cu}^{2+}$ ) is surrounded by four oxygen ions ( $\text{O}^{2-}$ ). These planes are held together in the structure by calcium ( $\text{Ca}^{2+}$ ) ions located between them, as indicated in Fig. 8.3. An exception to this is the yttrium compound in which the intervening ions are the element yttrium ( $\text{Y}^{3+}$ ) instead of calcium. These  $\text{CuO}_2$  planes are very close to being flat. In the normal state above  $T_c$ , conduction electrons released by copper atoms move about on these

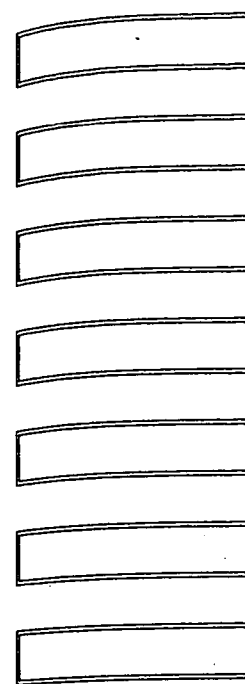


Figure 8.1. Layering scheme for different sequences for several cuprates.

Figure 8.2. Arrangement in a  $\text{CuO}_2$  plane of the con

Transition Temperature  $T_c$   
in 1986

Year
1986
1986
1987
1988
1988
1993
1993
1994

t, a high-transition temperature superconductor useful for applications in magnets, they must be able to have high critical current density as those in niobium-tin superconductors that can easily be made in thin films on various substrates.

At a temperature much above the critical temperature, the superconductor must operate significantly below the critical magnetic field  $B_c$ . At low temperature, the critical magnetic field is about 0.4 and 3.5 that  $B_c$  and  $J_c$  are low. We need an operating temperature so that both  $B_c$  and  $J_c$  are high.

## ES

As shown in Fig. 8.1: The superconducting binding layers support the conduction layers which contain copper-oxide. The copper ion ( $\text{Cu}^{2+}$ ) is surrounded in the structure by calcium ions. An exception to this is the element yttrium ( $\text{Y}^{3+}$ ) which is being flat. In the normal state, the ions move about on these

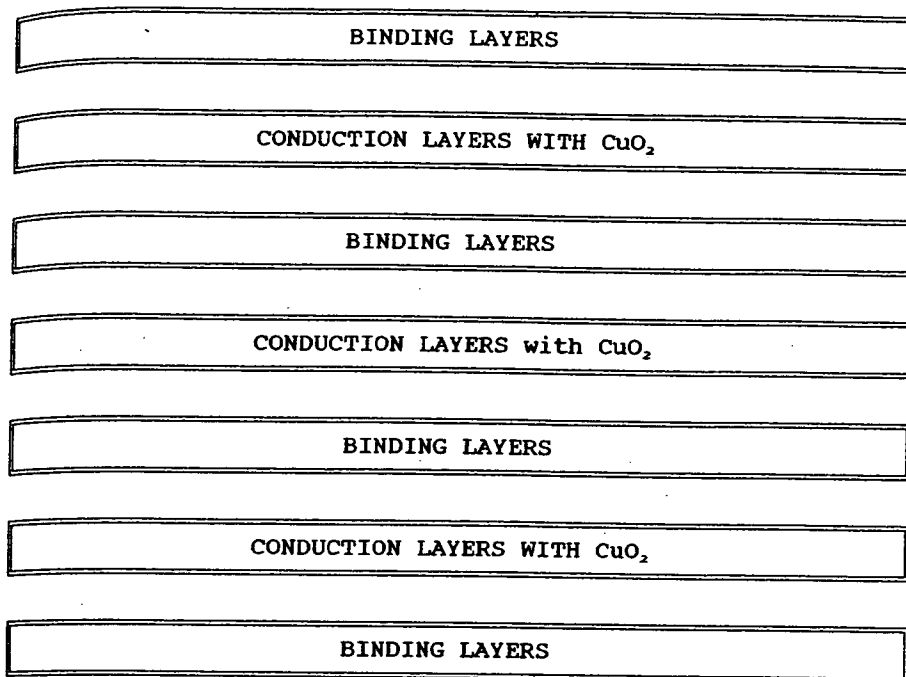


Figure 8.1. Layering scheme of the cuprate superconductors. Figure 8.3 shows details of the conduction layers for different sequences of copper oxide planes, and Fig. 8.4 presents details of the binding layers for several cuprates.

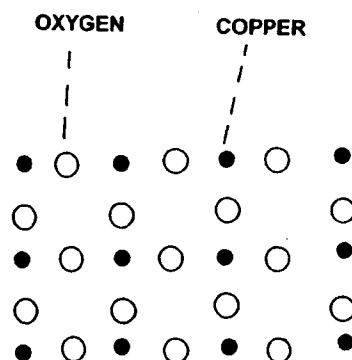
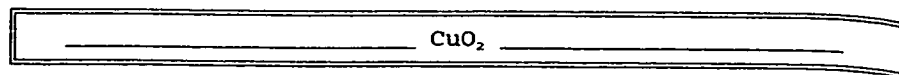
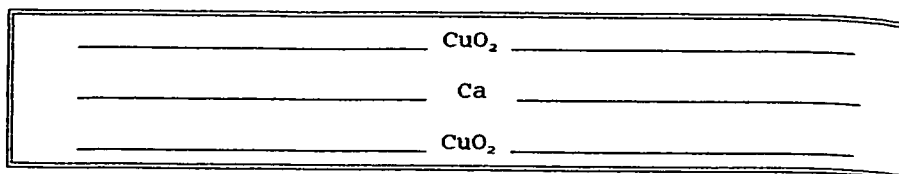


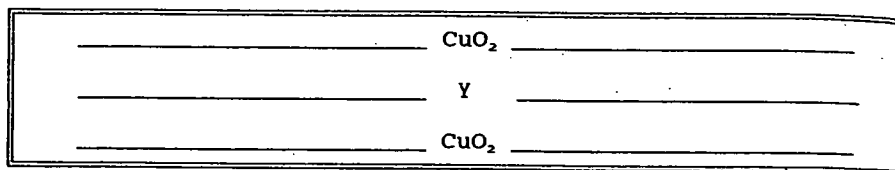
Figure 8.2. Arrangement of copper and oxygen atoms in a  $\text{CuO}_2$  plane of the conduction layer.



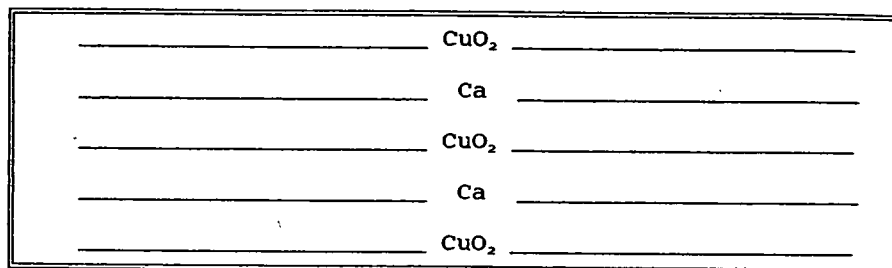
Conduction layer with one copper oxide plane



Conduction layer with two copper oxide planes



Conduction layer of yttrium compound with two copper oxide planes

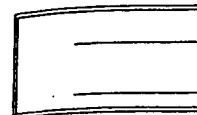
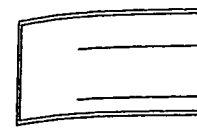


Conduction layer with three copper oxide planes

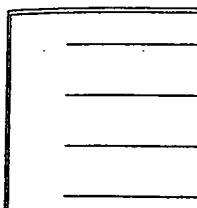
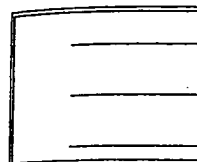
Figure 8.3. Conduction layers of the various cuprate superconductors showing sequences of  $\text{CuO}_2$  and Ca (or Y) planes in the conduction layers of Fig. 8.1.

$\text{CuO}_2$  planes carrying electric current. In the superconducting state below  $T_c$ , these same electrons form the Cooper pairs that carry the supercurrent in the planes.

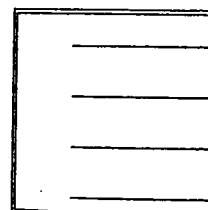
Each particular cuprate compound has its own specific binding layer consisting mainly of sublayers of metal oxides MO, where M is a metal atom; Fig. 8.4 gives the sequences of these sublayers for the principal cuprate compounds. These binding layers are sometimes called *charge reservoir layers* because they contain



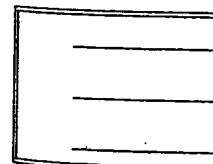
Neodyn



Bismu



Thalli



Mercur

Figure 8.4. Sequences of metal ions. The parent

# CHAPTER 8

oxide plane

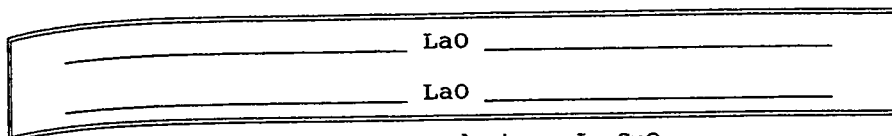
oxide planes

two copper oxide planes

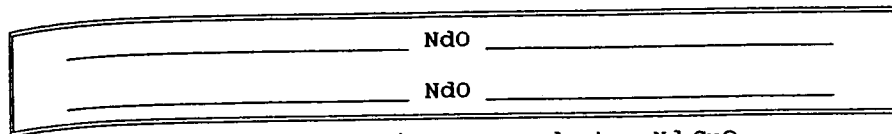
oxide planes

ctors showing sequences of  $\text{CuO}_2$  and

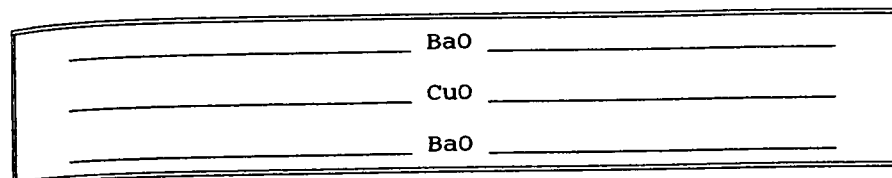
conducting state below  $T_c$ , these supercurrent in the planes. specific binding layer consisting is a metal atom; Fig. 8.4 gives 1 cuprate compounds. These *ir layers* because they contain



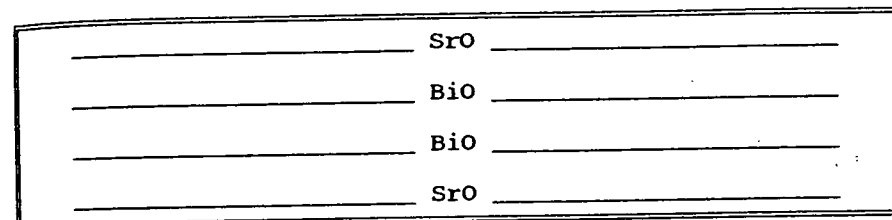
Lanthanum Superconductor  $\text{La}_2\text{CuO}_4$



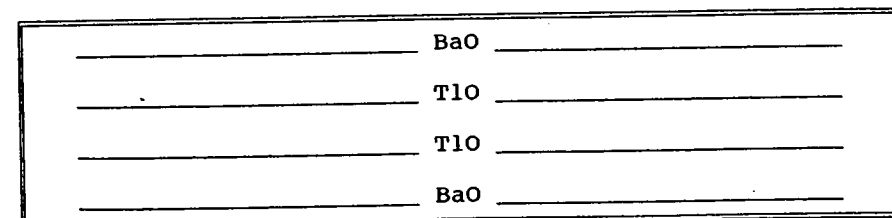
Neodymium (electron) Superconductor  $\text{Nd}_2\text{CuO}_4$



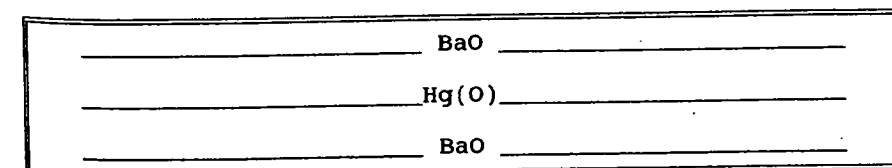
Yttrium Superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_7$



Bismuth Superconductor  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$



Thallium Superconductor  $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$



Mercury Superconductor  $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2}$

Figure 8.4. Sequences of MO sublayers in the binding layers of Fig. 8.1, where M stands for various metal ions. The parentheses around the oxygen atom O in the lowest panel indicates partial occupancy.

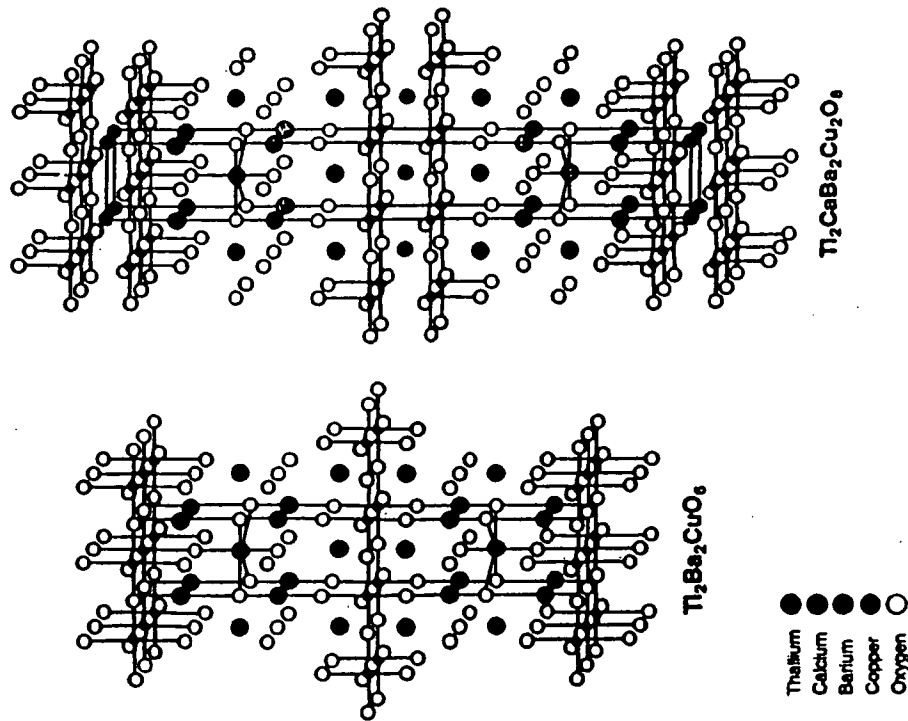


Figure 8.5. Layering schemes of three thallium compound superconductors  $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+6}$  where there are  $n = 1, 2, 3$   $\text{CuO}_2$  planes in the conduction layers, from left to right. (Adapted from Toraldi et al., *Science* 240, 631 (1988).)

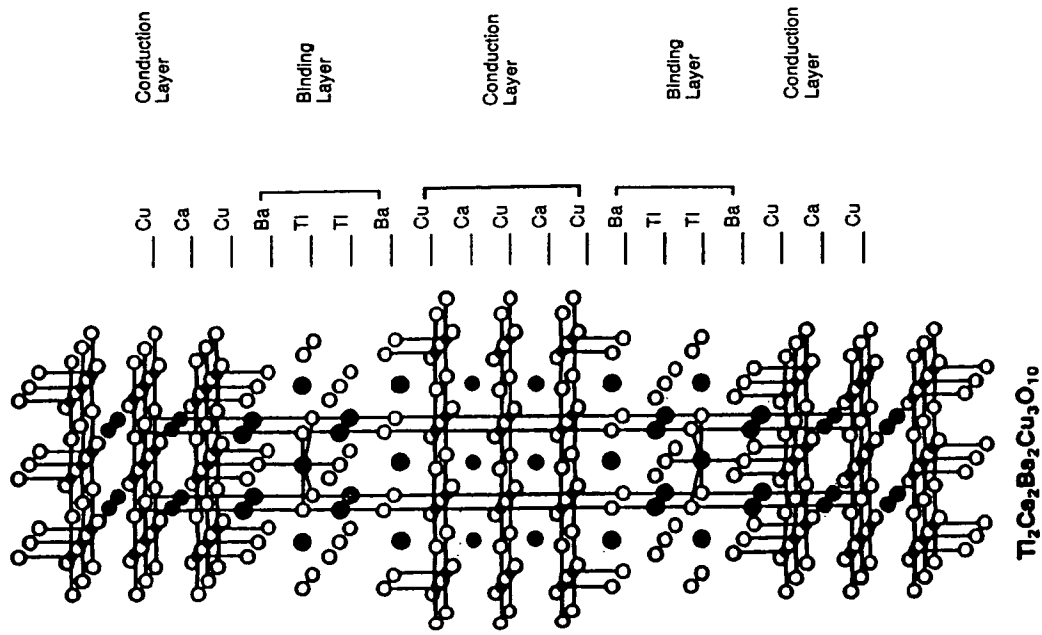


Figure 8.5. (Continued)

of randomly oriented grains. In the current flow capability of

$\text{La}_{1-x}\text{Sr}_x\text{CuO}_4$  are hole-type cerium-copper oxide,  $(\text{Nd}_{1-x}\text{Ce}_x)_2\text{CuO}_4$  contains trivalent positive ions:

(8.6)

(8.7)

tium ( $\text{Sr}^{2+}$ ) and cerium ( $\text{Ce}^{4+}$ ),

$\text{La}_2\text{CuO}_4$  (8.8)

$\text{La}_2\text{CuO}_4$  (8.9)

one extra electron to form an antiferromagnet. Lanthanum ion subtracts one electron, superconductor is hole-like. Any material both of these examples of perovskite, but not identical structures; because most experiments are not

## STRUCTURES

referred to as ceramics, they are perovskite refers to the particular mineral perovskite, calcium titanate. The structure of the lanthanum compound  $\text{La}_2\text{CuO}_4$  is perovskite-type, with Cu present in the positions not shown in Fig. 8.9) positions. Similarities between these two compounds and  $\text{La}_2\text{CuO}_4$  a perovskite-type

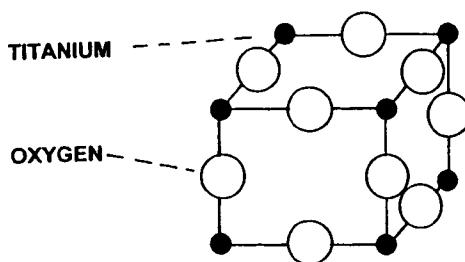


Figure 8.9. Sketch of the cubic unit cell of the mineral Perovskite,  $\text{CaTiO}_3$ , showing titanium at the vertices and oxygen in the middle of the edges. Calcium, not shown, is in the center of the cube.

In contrast the ceramic designation is not based on structural grounds but on the similarity of the cuprate-superconducting compound and ceramic manufacturing process. For example  $\text{La-Sr-Cu-O}$  is made by heating mixtures of lanthanum oxide, strontium carbonate, and copper oxide in air at  $900\text{--}1000^\circ\text{C}$  for 20 hours. Proportions of atoms in the initial mixture should be the same as in the end product, and for the compound  $(\text{La}_{0.9}\text{Sr}_{0.1})_2\text{CuO}_4$  the ratio  $\text{La}:\text{Sr}:\text{Cu}$  is 1.8:0.2:1. Materials are usually ground to a fine mixture before heating; after heating in air, they are cooled, pressed into pellets, and reheated from  $900\text{--}1000^\circ\text{C}$  for several more hours.

We see in Fig. 8.10 that the superconductor  $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4$  has only one copper oxide plane in its conduction layer and each copper ion is surrounded by

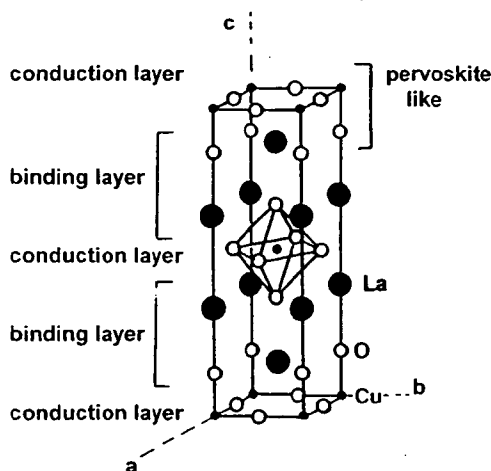


Figure 8.10. Atom positions in the tetragonal unit cell of the  $\text{La}_2\text{CuO}_4$  compound. When strontium is substituted for lanthanum in the superconducting compound  $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4$  it replaces lanthanum in some of the La sites.





# **BRIEF ATTACHMENT AH**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of

Applicants: Bednorz et al.

Serial No.: 08/479,810

Filed: June 7, 1995

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Date: March 1, 2004

Docket: YO987-074BZ

Group Art Unit: 1751

Examiner: M. Kopec

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

**FIFTH SUPPLEMENTAL AMENDMENT**

Sir:

In response to the Office Action dated February 4, 2000:

**ATTACHMENT 16**

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of  
J. Bednorz et al.

Date: December 15, 1998

Serial No. 08/303,561

Group Art Unit: 1105

Filed: September 9, 1994

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

AFFIDAVIT UNDER 37 C.F.R. 1.132

Commissioner of Patents and Trademarks  
Washington, D. C. 20231

Sir:

I, David B. Mitzi, being duly sworn, do hereby depose and state:

That I received a B. S. E. degree in Electrical Engineering/Engineering Physics (1985) from Princeton University and a PhD. degree, in Applied Physics (1990) from Stanford University, California.

That I have worked as a research staff member in Solid State Chemistry at the Thomas Watson Research Center of the International Business Machines Corporation in Yorktown Heights, NY from 1990 to the present.

That I have worked in the fabrication of and characterization of high temperature superconductor and related materials from 1990 to the present.

That I have reviewed the above-identified patent application and that I have reviewed the above-identified patent application and acknowledge that it represents the work of Bednorz and

YO987-074BY

Muller, which is generally recognized as the first discovery of superconductivity above 26°K and that subsequent developments in this field have been based on this work.

That all the high temperature superconductors which have been developed based on the work of Bednorz and Muller behave in a similar manner, conduct current in a similar manner and have similar magnetic properties.

That once a person of skill in the art knows of a specific transition metal oxide composition which is superconducting above 26°K, such a person of skill in the art, using the techniques described in the above-identified patent application, which includes all known principles of ceramic fabrication known at the time the application was filed, can make the transition metal oxide compositions encompassed by the claims in the above identified application, without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art. This is why the work of Bednorz and Muller was reproduced so quickly after their discovery and why so much additional work was done in this field within a short period of their discovery.

The general principles of ceramic science referred to by Bednorz and Mueller in their patent application can be found in many books and articles published before their discovery. An exemplary list of books describing the general principles of ceramic fabrication are:

- 1) Introduction to Ceramics, Kingery et al., Second Edition, John Wiley & Sons, 1976, in particular pages 5-20, 269-319, 381-447 and 448-513, a copy of which is with the Affidavit of Thomas Shaw submitted December 15, 1998.
- 2) Polar Dielectrics and Their Applications, Burfoot et al., University of California Press, 1979, in particular pages 13-33, a copy of which is with the Affidavit of Thomas Shaw submitted December 15, 1998.
- 3) Ceramic Processing Before Firing, Onoda et al., John Wiley & Sons, 1978, the entire book, a copy of which is with the Affidavit of Thomas Shaw submitted December 15, 1998.

4) Structure, Properties and Preparation of Perovskite-Type Compounds, F.S. Glasco, Pergamon Press, 1969, in particular pages 159-186, a copy of which is with the Affidavit of Thomas Shaw submitted December 15, 1998.

An exemplary list of articles applying their general principles of ceramic fabrication to the types of materials described in applicants' specification are (these references are cited on applicant's 1449 form submitted August 5, 1987 and in PTO Form 892 in Paper # 20, Examiner's action dated August 8, 1990):

1) Oxygen Defect  $K_2NiF_4$  - Type Oxides: The Compounds  $La_{2-x}Sr_xCuO_{4-x/2+}$ , Nguyen et al., Journal of Solid State Chemistry 39, 120-127 (1981).

2) The Oxygen Defect Perovskite  $BaLa_4Cu_5O_{13.4}$ , A Metallic Conductor, C. Michel et al., Mat. Res. Bull., Vol. 20, pp. 667-671, 1985.

3) Oxygen intercalation in mixed valence copper oxides related to the perovskite, C. Michel et al., Revue de Chemie minerale, p. 407, 1984.

4) Thermal Behaviour of Compositions in the Systems  $x BaTiO_3 + (1-x) Ba(Ln_{0.5}B_{0.5})O_3$ , V.S. Chincholkar et al. Therm. Anal. 6th, Vol. 2., p. 251-6, 1980.

By: 

David B. Mitzi

Sworn to before me this 15<sup>th</sup> day of December, 1998

  
Notary Public

DANIEL P. MORRIS  
NOTARY PUBLIC, State of New York  
No. 4888876  
Qualified in Westchester County  
Commission Expires March 16, 1999

YO987-074BY

# **BRIEF ATTACHMENT AI**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of

Applicants: Bednorz et al.

Serial No.: 08/479,810

Filed: June 7, 1995

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Date: March 1, 2004

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Group Art Unit: 1751

Examiner: M. Kopec

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

**FIFTH SUPPLEMENTAL AMENDMENT**

Sir:

In response to the Office Action dated February 4, 2000:

**ATTACHMENT 17**



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of  
J. Bednorz et al. : Date: December 15, 1998

Serial No. 08/303,561 : Group Art Unit: 1105

Filed: September 9, 1994 : Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

AFFIDAVIT UNDER 37 C.F.R. 1.132

Commissioner of Patents and Trademarks  
Washington, D. C. 20231

Sir:

I, Timothy Dinger, being duly sworn, do hereby depose and state:

That I received a B. S. degree in Ceramic Engineering (1981) from New York State College of Ceramics, Alfred University, an M. S. degree (1983) and a PhD. degree (1986), both in Material Science from the University of California at Berkley.

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YO987-074BY

superconductivity above 26°K and that subsequent developments in this field have been based on this work.

That all the high temperature superconductors which have been developed based on the work of Bednorz and Muller behave in a similar way, conduct current in a similar manner and have similar magnetic properties.

That once a person of skill in the art knows of a specific transition metal oxide composition which is superconducting above 26°K, such a person of skill in the art, using the techniques described in the above-identified patent application, which includes all known principles of ceramic fabrication known at the time the application was filed, can make the transition metal oxide compositions encompassed by the claims in the above identified application, without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art. This is why the work of Bednorz and Muller was reproduced so quickly after their discovery and why so much additional work was done in this field within a short period of their discovery.

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By: Timothy A. Dinger  
Timothy Dinger

Sworn to before me this 16<sup>th</sup> day of December, 1998

Sandra M. Emma

Notary Public

SANDRA M. EMMA  
Notary Public, State of New York  
No. 01PO4935290  
Qualified in Westchester County  
Commission Expires July 5, 2000

# **BRIEF ATTACHMENT AK**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of

Applicants: Bednorz et al.

Serial No.: 08/479,810

Filed: June 7, 1995

Date: March 1, 2004

Docket: YO987-074BZ

Group Art Unit: 1751

Examiner: M. Kopec

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TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Commissioner for Patents  
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Alexandria, VA 22313-1450

**FIFTH SUPPLEMENTAL AMENDMENT**

Sir:

In response to the Office Action dated February 4, 2000:

**ATTACHMENT 19**

AK

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: J. Bednorz et al.

Date: December 15, 1998

Serial No. 08/303,561

Group Art Unit: 1105

Filed: September 9, 1994

Examiner: M. Kopec

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TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

**AFFIDAVIT UNDER 37 CFR 1.132**

Sir:

I, Thomas M. Shaw, being duly sworn, do hereby depose and state:

I received a B.S. degree in Metallurgy from the University of Liverpool, Liverpool, England and a M.S. and PhD. degree in Materials Science (1981) from the University of California, Berkeley.

I have worked as a postdoctoral researcher in the Material Science Department of Cornell University from 1981-1982. I worked at Rockwell International Science Center in Thousand Oaks, California from 1982-1984 as a ceramic scientist. I have worked as a research staff member in Ceramics Science at the Thomas J. Watson Research

Center of the International Business Machines Corporation in Yorktown Heights, N.Y.  
from 1984 to the present.

I have worked in the fabrication of and characterization of ceramic materials of various types, including superconductors and related materials from 1984 to the present.

Attached is a resume of my publications. I have reviewed the above-identified patent application and acknowledge that it represents the work of Bednorz and Mueller, which is generally recognized as the first discovery of superconductivity above 26°K and that subsequent developments in this field have been based on this work.

That all the high temperature superconductors which have been developed based on the work of Bednorz and Mueller behave in a similar manner, conduct current in a similar manner and have similar magnetic properties.

That once a person of skill in the art knows of a specific transition metal oxide composition which is superconducting above 26°K, such a person of skill in the art, using the techniques described in the above-identified patent application, which includes all known principles of ceramic fabrication known at the time the application was filed, can make the transition metal oxide compositions encompassed by the claims in the above-identified application, without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art. This is why the

work of Bednorz and Mueller was reproduced so quickly after their discovery and why so much additional work was done in this field within a short period of their discovery.

The general principles of ceramic science referred to by Bednorz and Mueller in their patent application can be found in many books and articles published before their discovery. An exemplary list of books describing the general principles of ceramic fabrication are:

- 1) Introduction to Ceramics, Kingery et al., Second Edition, John Wiley & Sons, 1976, in particular pages 5-20, 269-319, 381-447 and 448-513, a copy of which is attached herewith.
- 2) Polar Dielectrics and Their Applications, Burfoot et al., University of California Press, 1979, in particular pages 13-33, a copy of which is attached herewith.
- 3) Ceramic Processing Before Firing, Onoda et al., John Wiley & Sons, 1978, the entire book, a copy of which is attached herewith.
- 4) Structure, Properties and Preparation of Perovskite-Type Compounds, F.S. Glasco, Pergamon Press, 1969, in particular pages 159-186, a copy of which is attached herewith.

An exemplary list of articles applying their general principles of ceramic fabrication to the types of materials described in applicants' specification are (these references are cited on applicant's 1449 form submitted August 5, 1987 and in PTO Form 892 in Paper # 20, Examiner's action dated August 8, 1990):

- 1) Oxygen Defect  $K_2NiF_4$  - Type Oxides: The Compounds  $La_{2-x}Sr_xCuO_{4-x/2+\delta}$ , Nguyen et al., Journal of Solid State Chemistry 39, 120-127 (1981).
- 2) The Oxygen Defect Perovskite  $BaLa_4Cu_5O_{13.4}$ , A Metallic Conductor, C. Michel et al., Mat. Res. Bull., Vol. 20, pp. 667-671, 1985.



- 3) Oxygen intercalation in mixed valence copper oxides related to the perovskite, C. Michel et al., Revue de Chemie minerale, p. 407, 1984.
- 4) Thermal Behaviour of Compositions in the Systems  $x \text{BaTiO}_3 + (1-x) \text{Ba}(\text{Ln}_{0.5} \text{B}_{0.5}) \text{O}_3$ , V.S. Chincholkar et al. Therm. Anal. 6th, Vol. 2., p. 251-6, 1980.

By: Thomas M. Shaw  
Thomas M. Shaw

Sworn to before me this 14<sup>th</sup> day of December, 1998.

Sandra M. Emma  
Notary Public

SANDRA M. EMMA  
Notary Public, State of New York  
No. 01PO4935290  
Qualified in Westchester County  
Commission Expires July 5, 2000

# **BRIEF ATTACHMENT AJ**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of

Applicants: Bednorz et al.

Serial No.: 08/479,810

Filed: June 7, 1995

Date: March 1, 2004

Docket: YO987-074BZ

Group Art Unit: 1751

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

**FIFTH SUPPLEMENTAL AMENDMENT**

Sir:

In response to the Office Action dated February 4, 2000:

**ATTACHMENT 18**

AJ

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of  
J. Bednorz et al.

Date: December 15, 1998

Serial No. 08/303,561

Group Art Unit: 1105

Filed: September 9, 1994

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, AND METHODS FOR THEIR USE AND PREPARATION

AFFIDAVIT UNDER 37 C.F.R. 1.132

Commissioner of Patents and Trademarks  
Washington, D. C. 20231

Sir:

I, Chang C. Tsuei, being duly sworn, do hereby depose and state:

That I received a B. S. degree in Mechanical Engineering from National Taiwan University (1960) and M. S. and PhD. degrees, in Material Science (1963, 1966) respectively from California Institute of Technology.

That I have worked as a research staff member and manager in the physics of superconducting, amorphous and structured materials at the Thomas Watson Research Center of the International Business Machines Corporation in Yorktown Heights, New York from 1973 to the present. (See attached Exhibit A for other professional employment history.)

That I have worked in the fabrication of and characterization of high temperature superconductor and related materials from 1973 to the present.

That I have reviewed the above-identified patent application and acknowledge that it represents the work of Bednorz and Muller, which is generally recognized as the first discovery of  
YO987-074BY

superconductivity above 26°K and that subsequent developments in this field have been based on this work.

That all the high temperature superconductors which have been developed based on the work of Bednorz and Muller behave in a similar manner, conduct current in a similar manner and have similar magnetic properties.

That once a person of skill in the art knows of a specific transition metal oxide composition which is superconducting above 26°K, such a person of skill in the art, using the techniques described in the above-identified patent application, which includes all known principles of ceramic fabrication known at the time the application was filed, can make the transition metal oxide compositions encompassed by the claims in the above identified application, without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art. This is why the work of Bednorz and Muller was reproduced so quickly after their discovery and why so much additional work was done in this field within a short period of their discovery.

The general principles of ceramic science referred to by Bednorz and Mueller in their patent application can be found in many books and articles published before their discovery. An exemplary list of books describing the general principles of ceramic fabrication are:

- 1) Introduction to Ceramics, Kingery et al., Second Edition, John Wiley & Sons, 1976, in particular pages 5-20, 269-319, 381-447 and 448-513, a copy of which is with the Affidavit of Thomas Shaw submitted December 15, 1998.
- 2) Polar Dielectrics and Their Applications, Burfoot et al., University of California Press, 1979, in particular pages 13-33, a copy of which is with the Affidavit of Thomas Shaw submitted December 15, 1998.
- 3) Ceramic Processing Before Firing, Onoda et al., John Wiley & Sons, 1978, the entire book, a copy of which is with the Affidavit of Thomas Shaw submitted December 15, 1998.

4) Structure, Properties and Preparation of Perovskite-Type Compounds, F.S. Glasco, Pergamon Press, 1969, in particular pages 159-186, a copy of which is with the Affidavit of Thomas Shaw submitted December 15, 1998.

An exemplary list of articles applying their general principles of ceramic fabrication to the types of materials described in applicants' specification are (these references are cited on applicant's 1449 form submitted August 5, 1987 and in PTO Form 892 in Paper # 20, Examiner's action dated August 8, 1990):

- 1) Oxygen Defect  $K_2NiF_4$  - Type Oxides: The Compounds  $La_{2-x}Sr_xCuO_{4-x/2+}$ , Nguyen et al., Journal of Solid State Chemistry 39, 120-127 (1981).
- 2) The Oxygen Defect Perovskite  $BaLa_4Cu_5O_{13.4}$ , A Metallic Conductor, C. Michel et al., Mat. Res. Bull., Vol. 20, pp. 667-671, 1985.
- 3) Oxygen intercalation in mixed valence copper oxides related to the perovskite, C. Michel et al., Revue de Chemie minerale, p. 407, 1984.
- 4) Thermal Behaviour of Compositions in the Systems  $x BaTiO_3 + (1-x) Ba(Ln_{0.5}B_{0.5})O_3$ , V.S. Chincholkar et al. Therm. Anal. 6th, Vol. 2., p. 251-6, 1980.

By: Chang C. Tsuei  
Chang C. Tsuei

Sworn to before me this 16<sup>th</sup> day of December, 1998

Sandra M. Emma

Notary Public

SANDRA M. EMMA  
Notary Public, State of New York  
No. 01PO4935290  
Qualified in Westchester County  
Commission Expires July 5, 2000

YO987-074BY

CHANG C. TSUEI

Education

California Institute of Technology, M.S. (1963), Ph.D. (1966)

National Taiwan University, B.S. (1960)

Professional Employment

1993 - present - Research Staff Member

1983 - 1993 - Manager, Physics of Structured Materials

1979 - 1983 - Manager, Physics of Amorphous Materials

1974 - 1975 - Acting Manager, Superconductivity

1973 - 1979 - Research Staff Member

Harvard University: 1980 (Summer)

Visiting Scholar in Applied Physics

Stanford University: 1982 (Sept.) - 1983 (April)

Visiting Scholar in Applied Physics

California Institute of Technology

1972 - 1973 - Senior Research Associate in Applied Physics

1969 - 1972 - Senior Research Fellow in Materials Science

1966 - 1969 - Research Fellow in Materials Science

Exhibit A

YO987-074BY

# **BRIEF ATTACHMENT AK**



**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of

Applicants: Bednorz et al.

Serial No.: 08/479,810

Filed: June 7, 1995

Date: March 1, 2004

Docket: YO987-074BZ

Group Art Unit: 1751

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

**FIFTH SUPPLEMENTAL AMENDMENT**

Sir:

In response to the Office Action dated February 4, 2000:

**ATTACHMENT 19**

AK

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: J. Bednorz et al.

Date: December 15, 1998

Serial No. 08/303,561

Group Art Unit: 1105

Filed: September 9, 1994

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

**AFFIDAVIT UNDER 37 CFR 1.132**

Sir:

I, Thomas M. Shaw, being duly sworn, do hereby depose and state:

I received a B.S. degree in Metallurgy from the University of Liverpool, Liverpool, England and a M.S. and PhD. degree in Materials Science (1981) from the University of California, Berkeley.

I have worked as a postdoctoral researcher in the Material Science Department of Cornell University from 1981-1982. I worked at Rockwell International Science Center in Thousand Oaks, California from 1982-1984 as a ceramic scientist. I have worked as a research staff member in Ceramics Science at the Thomas J. Watson Research

Center of the International Business Machines Corporation in Yorktown Heights, N.Y.  
from 1984 to the present.

I have worked in the fabrication of and characterization of ceramic materials of various types, including superconductors and related materials from 1984 to the present.

Attached is a resume of my publications. I have reviewed the above-identified patent application and acknowledge that it represents the work of Bednorz and Mueller, which is generally recognized as the first discovery of superconductivity above 26°K and that subsequent developments in this field have been based on this work.

That all the high temperature superconductors which have been developed based on the work of Bednorz and Mueller behave in a similar manner, conduct current in a similar manner and have similar magnetic properties.

That once a person of skill in the art knows of a specific transition metal oxide composition which is superconducting above 26°K, such a person of skill in the art, using the techniques described in the above-identified patent application, which includes all known principles of ceramic fabrication known at the time the application was filed, can make the transition metal oxide compositions encompassed by the claims in the above-identified application, without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art. This is why the

work of Bednorz and Mueller was reproduced so quickly after their discovery and why so much additional work was done in this field within a short period of their discovery.

The general principles of ceramic science referred to by Bednorz and Mueller in their patent application can be found in many books and articles published before their discovery. An exemplary list of books describing the general principles of ceramic fabrication are:

- 1) Introduction to Ceramics, Kingery et al., Second Edition, John Wiley & Sons, 1976, in particular pages 5-20, 269-319, 381-447 and 448-513, a copy of which is attached herewith.
- 2) Polar Dielectrics and Their Applications, Burfoot et al., University of California Press, 1979, in particular pages 13-33, a copy of which is attached herewith.
- 3) Ceramic Processing Before Firing, Onoda et al., John Wiley & Sons, 1978, the entire book, a copy of which is attached herewith.
- 4) Structure, Properties and Preparation of Perovskite-Type Compounds, F.S. Glasco, Pergamon Press, 1969, in particular pages 159-186, a copy of which is attached herewith.

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- 1) Oxygen Defect  $K_2NiF_4$  - Type Oxides: The Compounds  $La_{2-x}Sr_xCuO_{4-x/2+\delta}$ , Nguyen et al., Journal of Solid State Chemistry 39, 120-127 (1981).
- 2) The Oxygen Defect Perovskite  $BaLa_4Cu_5O_{13.4}$ , A Metallic Conductor, C. Michel et al., Mat. Res. Bull., Vol. 20, pp. 667-671, 1985.

- 3) Oxygen intercalation in mixed valence copper oxides related to the perovskite, C. Michel et al., Revue de Chemie minerale, p. 407, 1984.
- 4) Thermal Behaviour of Compositions in the Systems  $x \text{BaTiO}_3 + (1-x) \text{Ba}(\text{Ln}_{0.5} \text{B}_{0.5}) \text{O}_3$ , V.S. Chincholkar et al. Therm. Anal. 6th, Vol. 2., p. 251-6, 1980.

By: Thomas M. Shaw  
Thomas M. Shaw

Sworn to before me this 14<sup>th</sup> day of December, 1998.

Sandra M. Emma  
Notary Public

SANDRA M. EMMA  
Notary Public, State of New York  
No. 01PO4935290  
Qualified in Westchester County  
Commission Expires July 5, 2000

# **BRIEF ATTACHMENT AL**

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Patent Application of

Applicants: Bednorz et al.

Serial No.: 08/479,810

Filed: June 7, 1995

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH TRANSITION  
TEMPERATURE, METHODS FOR THEIR USE AND PREPARATION

Date: March 1, 2004

Docket: YO987-074BZ

Group Art Unit: 1751

Examiner: M. Kopec

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

**FIFTH SUPPLEMENTAL AMENDMENT**

Sir:

In response to the Office Action dated February 4, 2000:

**ATTACHMENT 20**

AL

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

Applicants: J. Bednorz et al.

Date: December 18, 1998

Serial No. 08/303,561

Group Art Unit: 1105

Filed: September 9, 1994

Examiner: M. Kopec

For: NEW SUPERCONDUCTIVE COMPOUNDS HAVING HIGH  
TRANSITION TEMPERATURE, AND METHODS FOR THEIR  
USE AND PREPARATION

The Commissioner of Patents and Trademarks  
Washington, D.C. 20231

**AFFIDAVIT UNDER 37 CFR 1.132**

Sir:

I, Peter R. Duncombe, being duly sworn, do hereby depose and state:

I received a B.A. degree in Chemistry from the State University of New York at New Paltz, New Paltz, N.Y. and a M.S. degree in Chemical Engineering (1983) from the State University of New York at Buffalo, Buffalo, N.Y.

I have worked as a graduate research assistant in the Chemical Engineering Department of SUNY at Buffalo from 1980-1983. I have worked as a chemical engineer in Ceramics Science at the Thomas J. Watson Research Center of the International Business Machines Corporation in Yorktown Heights, N.Y. from 1984 to the present.



I have worked in the fabrication of and characterization of ceramic materials of various types, including superconductors and related materials from 1984 to the present.

Attached is a resume of my publications (Attachment A).

I have reviewed the above-identified patent application and acknowledge that it represents the work of Bednorz and Mueller, which is generally recognized as the first discovery of superconductivity above 26°K and that subsequent developments in this field have been based on this work.

That all the high temperature superconductors which have been developed based on the work of Bednorz and Mueller behave in a similar manner, conduct current in a similar manner and have similar magnetic properties.

That once a person of skill in the art knows of a specific transition metal oxide composition which is superconducting above 26°K, such a person of skill in the art, using the techniques described in the above-identified patent application, which includes all known principles of ceramic fabrication known at the time the application was filed, can make the transition metal oxide compositions encompassed by the claims in the above-identified application, without undue experimentation or without requiring ingenuity beyond that expected of a person of skill in the art. This is why the

work of Bednorz and Mueller was reproduced so quickly after their discovery and why so much additional work was done in this field within a short period of their discovery.

The general principles of ceramic science referred to by Bednorz and Mueller in their patent application can be found in many books and articles published before their discovery. An exemplary list of books describing the general principles of ceramic fabrication are:

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- 2) Polar Dielectrics and Their Applications, Burfoot et al., University of California Press, 1979, in particular pages 13-33, a copy of which is attached herewith.
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- 4) Structure, Properties and Preparation of Perovskite-Type Compounds, F.S. Glasco, Pergamon Press, 1969, in particular pages 159-181, a copy of which is attached herewith.

An exemplary list of articles applying their general principles of ceramic fabrication to the types of materials described in applicants' specification are (these references are cited on applicant's 1449 form submitted August 5, 1987 and in PTO Form 892 in Paper # 20, Examiner's action dated August 8, 1990):

- 1) Oxygen Defect  $K_2NiF_4$  - Type Oxides: The Compounds  $La_{2-x}Sr_xCuO_{4-x/2+\delta}$ , Nguyen et al., Journal of Solid State Chemistry 39, 120-127 (1981).
- 2) The Oxygen Defect Perovskite  $BaLa_4Cu_5O_{13.4}$ , A Metallic Conductor, C. Michel et al., Mat. Res. Bull., Vol. 20, pp. 667-671, 1985.

3) Oxygen intercalation in mixed valence copper oxides related to the perovskite, C. Michel et al., *Revue de Chemie minerale*, p. 407, 1984.

4) Thermal Behaviour of Compositions in the Systems  $x \text{BaTiO}_3 + (1-x) \text{Ba}(\text{Ln}_{0.5} \text{B}_{0.5}) \text{O}_3$ , V.S. Chincholkar et al. *Therm. Anal.* 6th, Vol. 2., p. 251-6, 1980.

I have recorded research notes relating to superconductor oxide (perovskite) compounds in technical notebook IV with entries from November 12, 1987 to June 14, 1988 and in technical notebook V with entries continuing from June 7, 1988 to May 2, 1989. Complete copies of each of these notebooks are attached - Attachment B - Book IV and Attachment C - Book V. Below is a listing of some of the compounds I prepared and recorded in these notebooks according to the teaching as described in the Bednorz and Mueller patent application using the general principles of ceramic science as described in the books and articles listed above.

In Book IV,  $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_x$  batch C1 pellet pressing, sintering notes and powder processing specifications start on page 2 and continue intermittently to pg. 40 (pg. 13 has superconductive susceptibility curves for pellet 9). Batch C2  $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_3$  detailed from pages 14 to 47.

In Book V green phase ( $\text{Y}_2\text{BaCuO}_x$ ) microstructural photomicrographs are logged on pages 15-17 with notes continuing to pg. 19. The perovskite superconductor  $\text{BiSrCaCu}$  oxide ( $\text{Bi}_{2.15}\text{Sr}_{1.68}\text{Ca}_{1.7}\text{Cu}_2\text{O}_{8+\delta}$ ) and related perovskites  $\text{Ca}_{(2-x)}\text{Sr}_x\text{CuO}_x$  and  $\text{Bi}_2\text{Sr}_2\text{CuO}_x$  synthesis notations start and continue through pg. 61 with microstructural photomicrographs.

A series of  $Y_1Ba_2Cu_3O_x$  stoichiometric perturbations to study compositional effects on 2nd phase or grain boundary phases and their effect on conductivity (resistivity), sintering behavior etc., continue until the end of the book notes on the page dated May 2, 1989 (page not numbered). These are typical perovskite synthetic procedures, microstructural photomicrographs, powder processing methods, characteristic susceptibility curve(s), sintering behavior and the like. Additional notes may be available in later notebooks.

The undersigned affiant swears further that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or patent issuing thereon.

By: Peter R. Duncombe  
Peter R. Duncombe

Sworn to before me this 18<sup>th</sup> day of December, 19 98.

Sandra M. Emma  
Notary Public

SANDRA M. EMMA  
Notary Public, State of New York  
No. 01PO4935290  
Qualified in Westchester County  
Commission Expires July 5, 2000

## ATTACHMENT A

1. Compensation doping of Ba<sub>0.7</sub>Sr<sub>0.3</sub>TiO<sub>3</sub> thin films  
Copel, M Baniecki, JD Duncombe, PR Kotecki, D  
Laibowitz, R Neumayer, DA Shaw, TM  
APPLIED PHYSICS LETTERS V73 N13 SEP 28 1998 P1832-1834
2. Method for Forming Noble Metal Oxides and Structures Formed Thereof. June 1998.  
Duncombe, P. R. Hummel, J. P. Laibowitz, R. B.  
Neumayer, D. A. Saenger, K. L. Schrott, A. G.  
RC 98A 41575
3. Growth of Bismuth Titanate Films By Chemical Vapor Deposition and Chemical Solution Deposition. March 1998. RC-21124  
Neumayer, D. A. Duncombe, P. R. Laibowitz, R. B.  
Shaw, T. Purtell, R. Grill, A.
4. Dielectric relaxation of Ba<sub>0.7</sub>Sr<sub>0.3</sub>TiO<sub>3</sub> thin films from 1 mHz to 20 GHz Baniecki, JD  
Laibowitz, RB Shaw, TM Duncombe, PR  
Neumayer, DA Kotecki, DE Shen, H Ma, QY  
APPLIED PHYSICS LETTERS V72 N4 JAN 26 1998 P498-500
5. Contrasting magnetic and structural properties of two La manganites with the same doping levels  
McGuire, T.R. Duncombe, P.R. Gong, G.Q. Gupta, A. Li, X.W. Pickart, S.J. Crow, M.L.  
J. Appl. Phys. (USA) Vol.83, No.11 1 June 1998 P7076-8
6. Effects of Annealing Conditions on Charge Loss Mechanisms in MOCVD (Ba<sub>0.7</sub>,Sr<sub>0.3</sub>)TiO<sub>3</sub> Thin Film Capacitors.  
Baniecki, J.D., Laibowitz, RB Shaw, TM Duncombe, PR Saenger, KL Cabral C  
Kotecki, DE , Shen, H , Lian, J., Ma, QY
7. Low Operating Voltage and High Mobility Field Effect Transistors Comproising Pentacene and Relatively High Dielectric Constant Insulators RC21233(94806) 7/17/98  
Dimitrakopoulos, CD Purushothaman S , Kymissis J. Callegari A. , Neumayer DA,  
Duncombe PR, Laibowitz RB, Shaw JM
8. Maximum Magnetoresistance in Granular Manganite/Insulator System close to Percolation Threshold PACS 10/06/98  
DK Petrov, L Krusin-Elbaum, JZ Sun, C Feild, & PR Duncombe
9. Magnetoresistance and Hall Effect of Chromium Dioxide Epitaxial Thin Films  
X.W. Li, A. Gupta, T.R. McGuire, P.R. Duncombe, Gang Xiao
10. Progress Report on High-k dielectric material: amorphous BST from solgel (09/98)  
P. Andry, D. Neumayer, P. Duncombe, C. Dimitrakopoulos, F. Libsch, A. Grill, R. Wisnieff

RC21352 (96175) 2 Dec 1998

SEND

MAIN  
MENU

OTHER  
OPTIONS

INCOMPLETE

## Personal Inventor History

Name: Duncombe, P.R.      Serial: 155139      Loc: RES YORKTOWN  
Patent Pts: 36      TDB Pts: 1      Total Pts: 37      Plateau Lvl: 3  
Plateau Date: 10/24/98      File Update: 11/02/98  
Awards Due: None

Title: NOVEL METAL ALKOXYALKOXIDECARBOXYLATES AND USE TO FORM FILMS

06/17/98 Opened as Discl YO8980231

Status: Filed

06/22/98 Discl Review

Action: File

① 09/04/98 Filed as Docket YO998254 in US      Rating: 2      Pts: 3  
Co-inventors: Neumayer, D.A.

Title: SELECTIVE GROWTH OF FERROMAGNETIC FILMS FOR MAGNETIC MEMORY, STORAGE-BASED DEVICES, AND OTHER DEVICES

06/17/98 Opened as Discl YO8980225

Status: Filed

06/29/98 Discl Review

Action: File

④ 10/15/98 Filed as Docket YO998268 in US      Rating: 2      Pts: 3  
Co-inventors: Guha, S. Gupta, A. Bojarczuk, N.A. Karasinski, J.M.

Title: BEOL DECOUPLING CAPACITOR MATERIALS

01/28/98 Opened as Discl YO8980024 in US

Status: Opened

06/24/98 Discl Review

Action: File

Co-inventors: Rosenberg, R. Ning, T.H. Shaw, T.M. Edelstein, D.C. Neumayer, D.A. Laibowitz, R.B.

③ "FABRICATION OF Strontium Bismuth Tantalate/Bismuth Titanate Multilayer Ferroelectric"  
Title: FERROELECTRIC THIN FILM STRUCTURES

10/01/97 Opened as Discl YO8970512 in US

Status: Opened

09/16/98 Discl Review

Action: File

② 10/30/98 SENT TO COUNSEL (L. Schires) Co-inventors: Shaw, T.M. Neumayer, D.A. Laibowitz, R.B.

Title: CAPACITORS WITH AMORPHOUS DIELECTRICS AND IMPROVED DIELECTRIC PROPERTIES MADE USING SILICON SURFACES AS ELECTRODES

06/06/97 Opened as Discl YO8970261 in US

Status: Opened

Co-inventors: Shaw, T.M. Neumayer, D.A. Laibowitz, R.B.

Title: FABRICATION OF THIN FILM FIELD EFFECT TRANSISTOR COMPRISING AN ORGANIC SEMICONDUCTOR AND CHEMICAL SOLUTION DEPOSITED METAL OXIDE

03/25/97 Opened as Discl YO8970113

Status: Filed

03/25/97 Discl Review

Action: File

03/25/97 Filed as Docket YO997083 in US

Rating: 2

Pts: 3

03/24/98 Filed as Docket YO997083 in JA

Rating: 2

03/16/98 Filed as Docket YO997083 in TA

Rating: 2

03/12/98 Filed as Docket YO997083 in KO

Rating: 2

04/24/98 Last Office Action

Co-inventors: Purushothaman, S. Dimitrakopoulos, C.D. Furman, B.K. Neumayer, D.A. Laibowitz, R.B.

Title: NOVEL ALKOXYALKOXIDES AND USE TO FORM FILMS

10/30/96 Opened as Discl YO8960411

Status: Filed

03/10/97 Discl Review

Action: File

⑤ 01/30/98 Filed as Docket YO997069 in US      Rating: 2      Pts: 3  
Co-inventors: Neumayer, D.A.

Title: THIN-FILM FIELD-EFFECT TRANSISTOR WITH ORGANIC SEMICONDUCTOR REQUIRING LOW OPERATING VOLTAGES

09/11/96 Opened as Discl YO8960358

Status:Filed

03/04/97 Discl Review

Action:File

03/25/97 Filed as Docket YO997057 in US

Rating: 2

Pts:3

03/12/98 Filed as Docket YO997057 in KO.

Rating: 2

04/10/98 Last Office Action

Co-inventors: Purushothaman, S. Dimitrakopoulos, C.D. Furman, B.K. Neumayer, D.A. Laibowitz, R.B.

X Title: HIGH DIELECTRIC CONSTANT, BARIUM LANTHANUM TITANATE THIN FILM CAPACITORS FOR RANDOM ACCESS

06/20/96 Opened as Discl YO8960255 in US

Status:Opened

Co-inventors: Gupta, A. Shaw, T.M. Laibowitz, R.B.

Title: METHOD FOR FORMING NOBLE METAL OXIDES AND STRUCTURES FORMED THEREOF

10/30/95 Opened as Discl YO8950450

Status:Filed

11/12/96 Discl Review

Action:File

11/05/97 Filed as Docket YO996239 in US

Rating: 2

Pts:3

10/20/98 Filed as Docket YO996239 in JA

Rating: 2

07/30/98 Filed as Docket YO996239 in TA

Rating: 2

Co-inventors: Schrott, A.G. Saenger, K.L. Hummel, J.P. Neumayer, D.A. Laibowitz, R.B.

Title: PEROXIDE ETCHANT PROCESS FOR PEROVSKITE-TYPE OXIDES

10/23/95 Opened as Discl YO8950434

Status:Filed

08/08/97 Discl Review

Action:File

04/08/98 Filed as Docket YO997256 in US

Rating: 2

Pts:3

Co-inventors: Rosenberg, R. Cooper, E.I. Laibowitz, R.B.

Title: RF TRANSPONDER FOR METALLIC SURFACES

08/02/95 Opened as Discl YO8950329 in US

Status:Opened

Co-inventors: Afzali-ardakani, A. Feild, C.A. Duan, D.W. Brady, M.J. Moskowicz, P.A.

Title: METHOD FOR CLEANING THE SURFACE OF A DIELECTRIC

09/06/95 Opened as Discl FI8950292

Status:Filed

09/06/95 Sent to Evaluator

02/05/96 Evaluated

Action:Search

04/19/96 Discl Review

Action:File

12/06/96 Filed as Docket FI996047 in US

Rating: 2

Pts:3

11/29/97 Filed as Docket FI996047 in KO

Rating: 2

05/26/97 Filed as Docket FI996047 in TA

Rating: 2

06/11/98 Last Office Action

Co-inventors: Kotecki, D.E. Wildman, H.S. Yu, C. Natzle, W. Laibowitz, R.B.

Title: NANO PHASE FABRICATION OF COPPER-GLASS CERAMIC COMPOSITE VIAS IN CORDIERITE SUBSTRATES

10/05/92 Opened as Discl YO8920907 in US

Status:Published

10/08/92 Sent to Evaluator

12/17/92 Discl Review

Action:Publish

01/06/93 Mailed to Tech Discl Bulletin

09/02/93 Published

Pts:1

Co-inventors: Kang, S.K. Shaw, T.M. Brady, M.J.

Title: METHOD OF SINTERING ALUMINUM NITRIDE

11/06/92 Opened as Discl FI8920668 in US

Status:Closed

11/06/92 Sent to Evaluator

12/18/92 Closed

Co-inventors: Takamori, T. Shinde, S.L.

Title: METHOD OF SINTERING ALUMINUM NITRIDE



11/06/92 Opened as Discl 18920667 in US Status: Closed  
11/06/92 Sent to Evaluator  
12/18/92 Closed  
Co-inventors: Takamori, T. Shinde, S.L.

Title: ALUMINUM NITRIDE BODY AND METHOD FOR FORMING SAID BODY UTILIZING A VITREOUS SINTERING ADDITIVE  
08/13/92 Opened as Discl FI8920525 Status: Filed  
08/17/92 Sent to Evaluator  
09/29/92 Evaluated Action: Search  
12/23/92 Discl Review Action: File  
05/10/95 Filed as Docket FI992168B in US Rating: 2 Pts: 3  
05/28/96 Issued as Patent 5520878 in US  
Co-inventors: Takamori, T. Shinde, S.L.

Title: ALUMINUM NITRIDE BODY AND METHOD FOR FORMING SAID BODY UTILIZING A VITREOUS SINTERING ADDITIVE  
08/13/92 Opened as Discl FI8920525 Status: Filed  
08/17/92 Sent to Evaluator  
09/29/92 Evaluated Action: Search  
12/23/92 Discl Review Action: File  
12/22/93 Filed as Docket FI992168A in US Rating: 2 Pts: 3  
01/09/96 Issued as Patent 5482903 in US  
Co-inventors: Takamori, T. Shinde, S.L.

Title: GOLD DOPING OF YBA2CU3O7-8 AS A MEANS OF INCREASING TRANSPORT CRITICAL CURRENT DENSITY  
02/12/92 Opened as Discl YO8920161 in US Status: Closed  
02/14/92 Sent to Evaluator  
05/15/92 Closed  
Co-inventors: Daeumling, M. Shaw, T.M.

Title: PROCESS FOR PRODUCING CERAMIC CIRCUIT STRUCTURES HAVING CONDUCTIVE VIAS  
07/19/89 Opened as Discl YO8890552 Status: Filed  
07/25/89 Sent to Evaluator  
08/10/89 Evaluated Action: Search  
07/30/90 Discl Review Action: File  
12/17/92 Filed as Docket YO990091B in US Rating: 2 Pts: 3  
08/16/94 Issued as Patent 5337475 in US  
Co-inventors: Vallabhaneni, R.V. Giess, E.A. Farooq, S. Cooper, E.I. Kim, Y.H. Vanhise, J.A. Aoude, F.Y. Muller-landau, F. Shaw, R.R. Walker, G.F. Rita, R.A. Neisser, M.O. Park, J.M. Shaw, T.M. Brownlow, J.M. Kim, J. Knickerbocker, S.H.

Title: VIA PASTE COMPOSITIONS AND USE THEREOF TO FORM CONDUCTIVE VIAS IN CIRCUITIZED CERAMIC SUBSTRATES  
07/19/89 Opened as Discl YO8890552 Status: Filed  
07/25/89 Sent to Evaluator  
08/10/89 Evaluated Action: Search  
07/30/90 Discl Review Action: File  
03/20/91 Filed as Docket YO990091A in US Rating: 2 Pts: 3  
02/01/94 Issued as Patent 5283104 in US  
Co-inventors: Vallabhaneni, R.V. Giess, E.A. Farooq, S. Cooper, E.I. Kim, Y.H. Vanhise, J.A. Aoude, F.Y. Muller-landau, F. Shaw, R.R. Walker, G.F. Rita, R.A. Neisser, M.O. Park, J.M. Shaw, T.M. Brownlow, J.M. Kim, J. Knickerbocker, S.H.

Call your award coordinator, IPL department, or T/L 826-2680 for help.

SEND

MAIN  
MENU

OTHER  
OPTIONS

- T.R. McGuire, A. Gupta, P.R. Duncombe, M. Rupp, J.Z. Sun, R.B. Laibowitz, W.J. Gallagher & G. Xiao "Magnetoresistance and Magnetic Properties of  $(\text{La}_{1-x})\text{MnO}_3$  Thin Films" 3M Conf. Proc: 4/96
- T.R. McGuire, P.R. Duncombe, G.Q. Gong, A. Gupta, X.W. Li & G. Xiao "Magnetoresistance & Magnetic Properties of  $(\text{La}_{1-x})\text{MnO}_3$  (Vacancy) Bulk Materials" 11/96 3M conf CMR Open Forum entry
- J.Z. Sun, L. Krusin-Elbaum, A. Gupta, G. Xiao, P.R. Duncombe, W.J. Gallagher & S. P. Parkin "Magneto-Transport in Doped Manganate Perovskites" 3M conference 11/12-15/96 Atlanta, Georgia
- P. Lecoeur, A. Gupta, P.R. Duncombe, G. Gong & G. Xiao "Emission Studies of the Gas-Phase Oxidation of Mn during Pulsed Laser Deposition Manganates in  $\text{O}_2$  &  $\text{N}_2\text{O}$  Atmospheres" JAP 80(1), 7/1/96
- J.Z. Sun, L. Krusin-Elbaum, A. Gupta, G. Xiao, P.R. Duncombe, W.J. Gallagher & S.S.P. Parkin "Colossal Magnetoresistance in Doped Manganate Perovskites" IBM J&D to appear 1996/97
- A. Gupta, G.Q. Gong, G. Xiao, P.R. Duncombe, P. Trouilloud, P. Lecoeur, Y.Y. Wang, V.P. Dravid, & J.Z. Sun "Grain Boundary Effects on the Magnetoresistance Properties of Perovskite Manganite Films"
- J.Z. Sun, W.J. Gallagher, P.R. Duncombe, L. Krusin-Elbaum, R.A. Altman, A. Gupta, Y. Lu, G.Q. Gong & G. Xiao "Observation of Large Low-field Magnetoresistance in Tri-layer Perpendicular Transport Devices Made Using Doped Manganate Perovskites" to appear Appl. Phys. Lett.
- J.Z. Sun, L. Krusin-Elbaum, P.R. Duncombe, A. Gupta & R. B. Laibowitz "Spin-Polarized Tunneling in Doped Perovskite Manganate Trilayer Junctions" APL submission 11/96
- T.R. McGuire, P.R. Duncombe, C.Q. Gong, A. Gupta, X.W. Li & G. Xiao "Interlayer Exchange Coupling & Magnetoresistance Of LCMO/LSMO 67/33 Multilayers" APL submission
- R.B. Laibowitz, T.M. Shaw, D.E. Kotecki, S. Tiwari, A. Gupta, A. Grill, & P.R. Duncombe "Properties and Applications of Thin Films of Lead Lanthanum Titanate (PLT) and Barium Strontium Titanate (BST) APS mtg 3/18-22/96
- P.R. Duncombe, S.L. Shinde, & T. Takamori "Aluminum Nitride Body Utilizing A Vitreous Sintering Additive" US05482903 1/9/96 (EF Plaque)
- P.R. Duncombe, S.L. Shinde, & T. Takamori "Aluminum Nitride Body & Method for Forming Said Body Utilizing a Vitreous Sintering Additive" US05520878 issued 5/28/96; I.A. Patent issue Award: 8/96
- Ali Afzali-Ardakani, Mike Brady, Dah-Wei Duan, Peter Duncombe, Chris Feild, and Paul Moskowitz "RF Transponder for Metallic Surfaces" Docket#: YO895-0329 submitted: 8/2/95
- D.E. Kotecki, R.B. Laibowitz, W. Natze, C. Yu, H. Wildman, P.R. Duncombe "Method for Cleaning the Surface of BST Prior to Electrode Deposition" Application #:FI996047 draft #1 under review
- E.I. Cooper, P.R. Duncombe, R.B. Laibowitz, "Peroxide Etchant Process for Titanate Dielectrics" Docket: YO895-0434 rated file; in prep.
- D.A. Neumayer, P.R. Duncombe, R.B. Laibowitz, & A. Grill "Sol-Gel Processing of  $\text{BaSrTiO}_3$  Films" submitted to International Symposium on Integrated Ferroelectrics (ISIF: 3/2-5/97) Santa Fe, N.M.
- A. Grill, R. Laibowitz, D. Beach, D. Neumayer & P.R. Duncombe "Effect of Base Electrode on the Crystallization & Electrical Properties of PLT" IBM RC 20402 (90185) 3/5/96
- D.A. Neumayer, P.R. Duncombe, R.B. Laibowitz & A. Grill "Effect of  $\text{TiO}_x$  Nucleation Layer on Crystallization of Sol-Gel Derived  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  Films" ISIF submission 3/97
- C.D. Dimitrakopoulos, P.R. Duncombe, B.K. Furman, R.B. Laibowitz, D. Neumayer, S. Purushothaman, J. Shaw "Field Effect Transistor for Low Voltage Operation" Disclosure YO896-0358 rated file: 9/11/96
- R.B. Laibowitz, P.R. Duncombe, D. Neumayer, K.L. Saenger, A.G. Schrott "Noble Metal Surfaces" YO896-04xx rated "file" 10/96
- T. Shaw, R.B. Laibowitz, P.R. Duncombe & A. Gupta "High Dielectric Constant Barium Lanthanum Titanate-Based DRAM Structures" Disclosure #: YO898-0681 rated File 5/96 in preparation
- D. Neumayer, P.R. Duncombe "Fabrication of Barium Strontium Titanate Films" YO896-04xx rated File 10/96 in preparation

IBM Commitments:

To Win

To Execute

To Teamwork

ATTACHMENT B

101001

Technical Notebook  
Book IV

User's Initials and Last Name:

P DUNCOMBE

Employee Serial:

15513P

Date of First Entry:

Date of Last Entry:

Security Classification:

11/12/87 6/88

MORAR

11/12

IBM Technical Notebook

1

70/30 - 25-25 } C1 GEP 2 - ~ 12:30 start

3.094<sup>?</sup> 0.574 0.179 4.07  
1.458 0.455 0.760

"63.9" 123 basis  
84.6!?

~4 hrs

3.047  
≤ ~1.5% loss

0.515 0.158  
1.308 0.401 0.539

5.65

88.7 better  
P1 → 83.4

11/12

11/13 SrTiO<sub>3</sub> - ST3 → 32 hrs ST2 pes. → 48

SrTiO<sub>3</sub> ⇒ ST3 ⇒ coded in morning see book III, pg (A7)

4.024 0.510 ✓ 0.240 ✓ ~ 5.01 "1.04(2)% dense"  
no airt loss 1.295 0.610 0.803 same Sally

~48 hrs (+ cooling 3 mornings, stepwise) sintering pellet

Cutting record

start 0.425 (0)

+ 0.060 Δ - saw (0.015) = 0.045 ~ 1.14 mm w/ flattening ~ 1 mm ✓  
0.485 (Δ 0) ↳ 0.042 (1.08 mm) OK

0.060  
0.545 (0.045 Δ resid; actual ⇒ 0.052 → 1.32 mm

(55)

0.0465 1.18 mm

0.0523

bottom (0.6-0.69) not flat 1.52 mm

The above understood

Date

and  
hv

Date

10/13  
 2

IBM Technical Notebook

PRE  
 STA - some deformity on 1 side (a slice worth)  
 4.178      0.584      ~0.287      3.316  
             1.483      0.729      1.26

way final piece of  
 ST2 @ 4.55  
68.9  
 average

will remove Monday morn: ~ 6:30 SAT, 6 SAT-6 SUN, ~ 63+ hours projected

10/16  
 4.169      0.510      ~0.250      4.98      1.035 <CONSISTENT>  
 (0.2%)      1.295      0.635      0.837

G1 ISO-26,000 - UCL-3300  
 4.01      0.578      0.248      0.542      3.96  
             1.468      0.630      ~~0.497~~  
                                  1.066  
 density est. (figure 65%) => 5.785 RANGE (5.37-6.27)

C1 ZF1  
 10/17 3300 / 26,000  
 3.105      0.566      0.193(4)      3.90      61.2%  
             1.438      0.490      0.796

G1 licks  
 3.985      0.578      0.250 (no change)      3.738 (lost 0.5% density)

10:18 in hot furnace, packed  $T_c$  - 520C  

	$T_c$	$T_s$	$T_{SET}$	
20	977	745	971	to 'push' $\Delta T$
21	↓	838	✓	
22		898		
23		935		
24		949	956	23 1/2 → 951
2:23				~ SET-PT.
2:54	435			"OFF" for slow-cool (first stepped to 840)

The above understood

Date

and

Date

IBM Technical Notebook

3

10/17

C1241 → pellet multiply cracked as if organic residue vaporized, evidence of vapor transport to support plate, etc. ex Na

2.925 80.18  
5.5%

9.79 - 3.105 ⇒ 6.685

10/18

G1 - post 4.044 split in 4 pieces (seem wet on cooling)

G2 4.1	0.579	0.253	3.75 ✓	pellet slightly disfigured, but ok.
	1.471	0.643	1.093	

33

4.155				
0.510	0.220		5.64	about expected density
1.295	0.559	0.736		

D.D.1 Pre  
3.10

0.5765" 0.191"

3.11

0.513	0.165		5.61	88.2
1.303	0.419	0.559		

5.75

4  
11/24

IBM Technical Notebook

Thermodyne Tube furnace set-up specs.

thermocouple: dia. ~0.255 length 20" + USED 23"

Set-up complete w/ plug in jacks, ext. wire, 5 couples.

11/30 Analytical Submissions

C1 - 0.75 g	$Y_{0.02} Ba_{0.98} Cu_{0.6}$	$Y, Ba, Cu$
C2 - 1.1	$Y_2O_3$	$Y$ , trace 99%
C3 - 2.0	$BaO$	$Ba$ ,
C4 - 1.0	$TiO_2$	$Ti$ , trace
C5 - 2.0	$SrTiO_3$ pre	$Sr, Ti$ , trace
C6 - 1.0	↓ post mill	↓
C7 2.0	DRC 123.	$Y, Ba, Cu$
C8	DD 123	$Y, Ba, Cu$
C9	off comp 2.11	



IBM Technical Notebook

5

'New'  $30 \xrightarrow{20.25} g$  GRINDING CHARGE of  $SrTiO_3$  in mill (3:10)  
 $O_2$ , compressed AIR,  $CO_2$  cylinders obtained w/ regulations off (4:17)  
 Ar

YIELD  $\rightarrow 20.4 g$   $\therefore$  MUST be some from old batch or  $ZrO_2$   
 COMBINED w/ OLD PWDR  $\rightarrow 23 g$  of milled powder

12/2 C1. batch 45.6 grams left  
 $39.56 g$  (rib g kept for files)  
 $\frac{10.5}{29.5}$  left for pellets  
 $\sim 10$  for grinding charge TFE/Toluene

NEW BOTTLES ORDERED, NO TEFLON AVAILABLE, - approx - 60 hrs total

$SrTiO_3$  pellets  $\rightarrow 10-10$  (29 hrs) down 1  $\therefore 2-2$  (12?)  $\sim 12-12$  (24) Thus

ST5, ST6 - start 10 A.M. 12/8, numerous interruptions due to furnace malfunctions, out 12:00 P.M. 12/10  
 ST5 edge chips 1 side OK otherwise 21 ISO.

\* 4.08 0.285 0.584  
 0.52

(01) 0.237 0.520 4.94 1.027  
 0.602 1.321 0.825

ST6 large chip during iso pressing in  $3/4$  side, must do

4.128 0.586 0.886  
~~0.520~~ ~~0.825~~

4.15 0.513 0.249 4.92 1.023  
 1.303 0.632(5) 0.843

\* bisecting crack

The above understood

Date

and

Date

6

IBM Technical Notebook

950C Run

POST GREEN	C1P9	3.108	0.577	0.185	3.92	61.5
			1.466	0.470	0.793	
POST GREEN	3.1	0.514	0.161	5.66	88.9%	
	no loss	1.306	0.409	0.548		
POST GREEN	DRC 2	0.579	0.177	4.19	65.8	
	3.204	1.471	0.450	0.765		
POST	3.2	0.551	0.165	4.96	77.9	
	no loss	1.400	0.419	0.645		

7/7

pellets not in best shape after 50 st, 26000

975C Run

POST	C1P10	0.574	0.185	3.99	61.8	
	3.090	1.458	0.470	0.785		
POST	3.056	0.508	0.157	5.88	92.3	PROBABLY 93
	1% loss	1.288	0.399	0.510	+3.4%	

* DRC 3	0.579	0.181	4.24	66.6% ~	
	3.318	1.471	0.460	0.782	

POST	crack still apparent, but holding	3.293	0.547	0.168	0.647	5.08	79.9 + 2%
	0.75% loss	0.389	0.427				

C1P10 Pyrometer 91.8 → 92 ∴ mostly closed porosity (95% of on peak density basis)

\* cracked in 1/2, but holding. Will go w/ see if it heats.

To Temp @ 4:05 → 2 HRS 6:05, then ramp down

4:00 P.M. 12/8 start cooling, OK NOT FLOWING WHEN ARRIVED, THOUGH COULD HAVE HAD BACK PRESSURE

IBM Technical Notebook

7/3 7

12-8

100% E/G mix  $\Rightarrow$  new wght calc.

(4.0 g) E basis (transferred to jar for physical mixing)

$$92.0913 \text{ g / mM section} \therefore \frac{4.0}{92.0913} = 0.0434 \text{ mM}$$

0.0434 mM is BASIS for mix of 0.7 mM E ectetic

$$0.0434 / 0.7 = 0.0620 \text{ mM total} \therefore 0.3 \text{ mM } \underline{211}$$

$$0.3 (0.0620) = 0.0186 \text{ mM } (94.6725 \text{ g / mM } 211) = \underline{1.761 \text{ g } 211}$$

$$\begin{array}{r} 1.761 \text{ g } 211 \\ 4.0 \text{ g } E \\ \hline 5.76(1) \text{ g mix} \end{array}$$

$$\text{tare } 0.83 \quad \begin{array}{r} 5.76 \\ 5.68 \text{ recovered} \\ \hline 0.08 \text{ g loss on mixing} \end{array}$$

5.53 after gundng (light loss on transfer)

1 pellet pressed  $\Rightarrow$  EG1  $\Rightarrow$  to temp 12/10 @ 3:40-45 NOT OUT TO BE 5:45

$$\begin{array}{r} 2.57 \quad 0.580 \quad 0.153 \quad 3.88 \quad "60.9" \rightarrow 74\%? \\ 1.473 \quad 0.389 \quad 0.663 \end{array}$$

Rel. density calc  $0.3 (6.00) + 0.7 (4.9) \Rightarrow 5.23$  approx theoretical  
 $\uparrow$  EMPIRICAL'S

$$\begin{array}{r} 2.543 \quad \sim 0.611 \quad 0.161 \quad 2.825 \\ (1\% \text{ wght loss}) \quad 1.55 \quad 0.480 \quad 0.90 \end{array}$$

Restarted for overite RUN

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# IBM Technical Notebook

## III. DENSITY WORKSHEET

### STEREOPHOTOGRAPHIC TRUE POWDER DENSITY

SAMPLE I.D. 660 DATE 12-9-87  
SOURCE DEC OPERATOR PRD  
TOTAL WEIGHT 18.855 g. OUTCASSING CONDITIONS  
TARE WEIGHT 4.061 g.  
SAMPLE WEIGHT 14.794 g.  
ADDED VOLUME,  $V_A$  cc  
CELL HOLDER VOLUME,  $V_C$  cc

$$\text{OPERATIONAL EQUATION } V_p = V_c \cdot \left[ \frac{V_A}{1 - P_2/P_3} \right]$$

$V_p$  = Volume of Powder (cc)  
 $V_c$  = Volume of Sample Cell Holder (cc)  
 $V_A$  = Added Volume  
 $P_2$  = Pressure Reading after Pressurizing Cell  
 $P_3$  = Pressure Reading after Added  $V_A$

DATA	RUN 1	RUN 2
$P_2$	18.362	18.488
$P_3$	4.980	5.013
$V_A$	7.023 cc	3.024 cc
DENSITY	4.89 g/cc	4.88 g/cc

$\pm 0.24$  (6%)  
 $4.85 \pm 5.13$   
{pressure}

## III. DENSITY WORKSHEET

### STEREOPHOTOGRAPHIC TRUE POWDER DENSITY

SAMPLE I.D. 660 DATE 12-9-87  
SOURCE DEC OPERATOR PRD  
TOTAL WEIGHT 12.606 g. OUTCASSING CONDITIONS  
TARE WEIGHT 4.061 g.  
SAMPLE WEIGHT 8.545 g.  
ADDED VOLUME,  $V_A$  cc  
CELL HOLDER VOLUME,  $V_C$  cc

$$\text{OPERATIONAL EQUATION } V_p = V_c \cdot \left[ \frac{V_A}{1 - P_2/P_3} \right]$$

$V_p$  = Volume of Powder (cc)  
 $V_c$  = Volume of Sample Cell Holder (cc)  
 $V_A$  = Added Volume  
 $P_2$  = Pressure Reading after Pressurizing Cell  
 $P_3$  = Pressure Reading after Added  $V_A$

DATA	RUN 1	RUN 2
$P_2$	18.310	18.502
$P_3$	5.078	5.213
$V_A$	-	1.296 cc
DENSITY	4.15 g/cc	3.96 g/cc

$\pm 0.3$   
 $3.96$   
 $5.15$

## III. DENSITY WORKSHEET

### STEREOPHOTOGRAPHIC TRUE POWDER DENSITY

SAMPLE I.D. 211 DATE 12-9-87  
SOURCE DEC OPERATOR PRD  
TOTAL WEIGHT 19.662 g. OUTCASSING CONDITIONS  
TARE WEIGHT 4.061 g.  
SAMPLE WEIGHT 15.601 g.  
ADDED VOLUME,  $V_A$  cc  
CELL HOLDER VOLUME,  $V_C$  cc

$$\text{OPERATIONAL EQUATION } V_p = V_c \cdot \left[ \frac{V_A}{1 - P_2/P_3} \right]$$

$V_p$  = Volume of Powder (cc)  
 $V_c$  = Volume of Sample Cell Holder (cc)  
 $V_A$  = Added Volume  
 $P_2$  = Pressure Reading after Pressurizing Cell  
 $P_3$  = Pressure Reading after Added  $V_A$

DATA	RUN 1	RUN 2
$P_2$	18.557	18.828
$P_3$	5.084	5.085
$V_A$	2.578 cc	2.736 cc
DENSITY	6.05 g/cc	6.080 g/cc

$\pm 0.3$   
 $(5.05 - 6.35)$   
 $\pm 0.24$   
 $(6.05 - 6.35)$

$\pm 0.2$   
 $6.00$

### STEREOPHOTOGRAPHIC TRUE POWDER DENSITY

SAMPLE I.D. 123 DATE 12-9-87  
SOURCE DEC OPERATOR PRD  
TOTAL WEIGHT 21.026 g. OUTCASSING CONDITIONS  
TARE WEIGHT 4.061 g.  
SAMPLE WEIGHT 16.965 g.  
ADDED VOLUME,  $V_A$  cc  
CELL HOLDER VOLUME,  $V_C$  cc

$$\text{OPERATIONAL EQUATION } V_p = V_c \cdot \left[ \frac{V_A}{1 - P_2/P_3} \right]$$

$V_p$  = Volume of Powder (cc)  
 $V_c$  = Volume of Sample Cell Holder (cc)  
 $V_A$  = Added Volume  
 $P_2$  = Pressure Reading after Pressurizing Cell  
 $P_3$  = Pressure Reading after Added  $V_A$

DATA	RUN 1	RUN 2
$P_2$	18.598	18.596
$P_3$	5.078	5.078
$V_A$	2.73 cc	-
DENSITY	6.21 g/cc	-

The above understood  
and understood by

Date

and

Date

12/9

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## III. DENSITY WORKSHEET

### STANDARDIZATION TRUE POWDER DENSITY

SAMPLE I.D. 123-344 DATE 12-9  
SOURCE DVAADS OPERATOR PRD  
TOTAL WEIGHT 19.700 g. OUTCASSING CONDITIONS  
TARE WEIGHT 4.061 g.  
SAMPLE WEIGHT 15.639 g. ADDED VOLUME,  $V_A$  18.57 cc  
CELL HOLDER VOLUME,  $V_C$  34.8 cc

$$\text{OPERATIONAL EQUATION } V_p = V_c \cdot \left[ \frac{V_A}{1 - P_2/P_1} \right]$$

$V_p$  = Volume of Powder (cc)  
 $V_c$  = Volume of Sample Cell Holder (cc)  
 $V_A$  = Added Volume  
 $P_1$  = Pressure Reading after Pressurizing Cell  
 $P_2$  = Pressure Reading after Added  $V_A$

R=3.646

DATA  
ROW 1  
ROW 2  
ROW 3

ROW 1	ROW 2	ROW 3
$P_1$ <u>18.603</u>	<u>18.561</u>	<u>18.561</u>
$P_2$ <u>5.103</u>	<u>5.091</u>	<u>5.091</u>
$V_p$ <u>2.523</u> cc	cc	cc
DENSITY <u>6.199</u> g/cc	g/cc	g/cc

no page

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## III. DENSITY WORKSHEET

### STANDARDIZATION ROW 2 TRUE POWDER DENSITY

SAMPLE I.D. 123 DATE 12-9  
SOURCE C1 OPERATOR PRD  
TOTAL WEIGHT 22.949 g. OUTCASSING CONDITIONS  
TARE WEIGHT 4.061 g.  
SAMPLE WEIGHT 18.888 g. ADDED VOLUME,  $V_A$  34.85 cc  
CELL HOLDER VOLUME,  $V_C$  34.85 cc

$$\text{OPERATIONAL EQUATION } V_p = V_c \cdot \left[ \frac{V_A}{1 - P_2/P_1} \right]$$

$V_p$  = Volume of Powder (cc)  
 $V_c$  = Volume of Sample Cell Holder (cc)  
 $V_A$  = Added Volume  
 $P_1$  = Pressure Reading after Pressurizing Cell  
 $P_2$  = Pressure Reading after Added  $V_A$

R=3.648

DATA

ROW 1	ROW 2	ROW 3
$P_1$ <u>18.508</u>		
$P_2$ <u>5.014</u>		
$V_p$ <u>3.087</u> cc	cc	cc
DENSITY <u>6.13</u> g/cc	g/cc	g/cc

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## III. DENSITY WORKSHEET

### STANDARDIZATION TRUE POWDER DENSITY

SAMPLE I.D. 123 DATE 12-9-87  
SOURCE C1-344 OPERATOR PRD  
TOTAL WEIGHT 19.959 g. OUTCASSING CONDITIONS  
TARE WEIGHT 4.063 g.  
SAMPLE WEIGHT 15.896 g. ADDED VOLUME,  $V_A$  18.57 cc  
CELL HOLDER VOLUME,  $V_C$  34.8 cc

$$\text{OPERATIONAL EQUATION } V_p = V_c \cdot \left[ \frac{V_A}{1 - P_2/P_1} \right]$$

$V_p$  = Volume of Powder (cc)  
 $V_c$  = Volume of Sample Cell Holder (cc)  
 $V_A$  = Added Volume  
 $P_1$  = Pressure Reading after Pressurizing Cell  
 $P_2$  = Pressure Reading after Added  $V_A$

R=3.58

DATA  
ROW 1  
ROW 2  
ROW 3

ROW 1	ROW 2	ROW 3
$P_1$ <u>18.677</u>	<u>18.643</u>	
$P_2$ <u>5.218</u>	<u>5.208</u>	
$V_p$ <u>1.703</u> cc	cc	cc
DENSITY <u>6.10</u> g/cc	<u>6.105</u> g/cc	g/cc

NOT BACK TO ZERO

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### STANDARDIZATION TRUE POWDER DENSITY

SAMPLE I.D. C1P10 DATE 12-10-87  
SOURCE C1-975782 OPERATOR PRD  
TOTAL WEIGHT 6.613 g. OUTCASSING CONDITIONS  
TARE WEIGHT 4.061 g.  
SAMPLE WEIGHT 2.552 g. ADDED VOLUME,  $V_A$  18.57 cc  
CELL HOLDER VOLUME,  $V_C$  34.8 cc

$$\text{OPERATIONAL EQUATION } V_p = V_c \cdot \left[ \frac{V_A}{1 - P_2/P_1} \right]$$

$V_p$  = Volume of Powder (cc)  
 $V_c$  = Volume of Sample Cell Holder (cc)  
 $V_A$  = Added Volume  
 $P_1$  = Pressure Reading after Pressurizing Cell  
 $P_2$  = Pressure Reading after Added  $V_A$

R=3.485

DATA  
ROW 1  
ROW 2  
ROW 3

ROW 1	ROW 2	ROW 3
$P_1$ <u>18.198</u>	<u>18.182</u>	
$P_2$ <u>5.208</u>	<u>5.217</u>	
$V_p$ <u>0.9355</u> cc	cc	cc
DENSITY <u>5.808</u> g/cc	g/cc	g/cc

6.10 → 95.6  
6.37 → 91.8 (92)

16

→ 16.48 + 58.715

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by

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10  
12/10

Powders for Analysis  $\Rightarrow$  Now entered @ conf. time  
12/11, SENSITIVITIES NOT ENOUGH  
Need to increase by 10X at least.

~~#1~~ - Species  
Description  
 $Y_2O_3$  left exposed to air

$TiO_2$

C1  $YBaCu$   
1 2 3

DD1

DRC

P11

EI

$Y_{0.02}Ba_{0.38}Cu_{0.6}$

off comp

off comp

Table I - Precision<sup>1</sup> of Metals determined by ICP in  $La_{1-x}Sr_xCuO_4$  and  $YBa_2Cu_3O_7$  Thin Films.

Element	$x^2$	S.D.	R.S.D. (%)
La	1.80	0.08	4.64
Sr	0.20	0.01	5.52
Cu	1.00	0.14	3.52
Y	1.00	0.05	5.60
Ba	2.04	0.07	3.43
Cu	3.00	0.11	3.67

<sup>1</sup>Based on 7 determinations

<sup>2</sup>Calculated atomic ratios

For 123

$Y (0.533) \Rightarrow \pm 0.019 \quad 0.314 - 0.352$

$Ba (0.667) \Rightarrow \pm 0.023 \quad 0.544 - 0.690$

$Cu (1.00) \Rightarrow \pm 0.036 \quad 0.963 - 1.0367$

Theoretical wgt % calcs.

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$TiO_2 \Rightarrow 47.90/79.8988 \rightarrow 59.95$

Anal 1

57.3

CRRE reported.

$SrCO_3 \Rightarrow 87.62/147.62935 \rightarrow 59.35$

ACT ANALYZED

$BaCO_3 \Rightarrow 137.34/197.34435 \rightarrow 69.59(2)$

$BaO \Rightarrow$

89.566

88.9

99.26 !

$SrTiO_3 \Rightarrow Sr \Rightarrow 47.74(5)$  M.W. 183.5182  
 $Ti \Rightarrow 26.10(1)$

(

C5- 22.2  
49.4

$Ti$   
 $Sr$

85.05% (15% poor)  
"3.48% rich"

C6 24.2  
50.6

$Ti$   
 $Sr$

92.72 (7.3% poor)  
"5.98% rich"

86.5

92.5

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12/14 both well shaped pellets

C1P11 - 15026

3.673      0.574      0.215      4.03      63.3  
1.458      0.546      0.9116

92+  from T. SHAW

C1fp(#)? 15026

3.058      0.560      0.200      3.606      56.6 as usual  
1.437      0.523      0.848

- final microstructure full of liquid, by metal g.s. } cracking
- no final density recorded

12/16 pellets in furnace from 12/14 in a purge.

To temp (10°C/min ramp from RT) @ 10:50 A.M.

Low (leading) side undershoot 974, high (downside) overshoot 978.

Stable variation 974-976 ✓

start ramp down 1:00 (12:50 p.m. (to 600C where soak for 48 hours)

$$\left\{ \text{Diff coef: } 2 \times 10^{-5} \text{ m}^2/\text{s}^{-1} \times 2 \times 10^{-15} \frac{\text{m}^2}{\text{s}^2} \times \frac{\text{ft}^2}{(0.3048 \text{ m})^2} = 2.153 \frac{\text{ft}^2}{\text{s}^2} \times 10^{-14} \right\}$$

The above understood  
and witnessed by \_\_\_\_\_

Date \_\_\_\_\_

and  
by \_\_\_\_\_

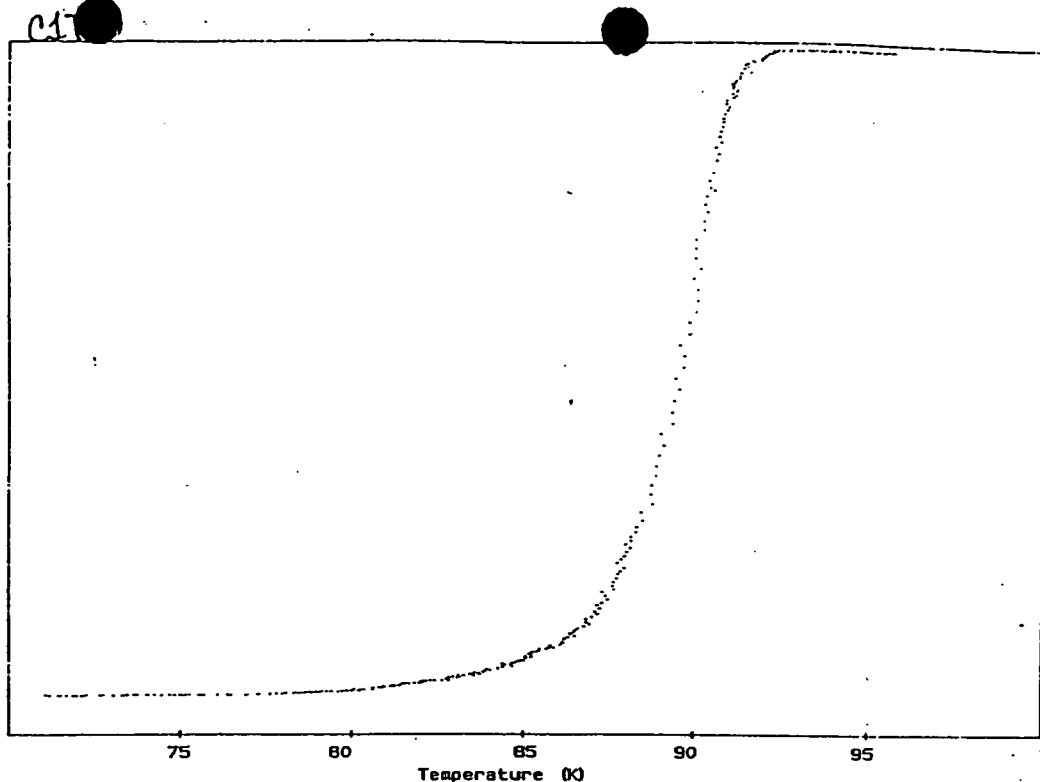
Date \_\_\_\_\_



0.00

$\Delta I$

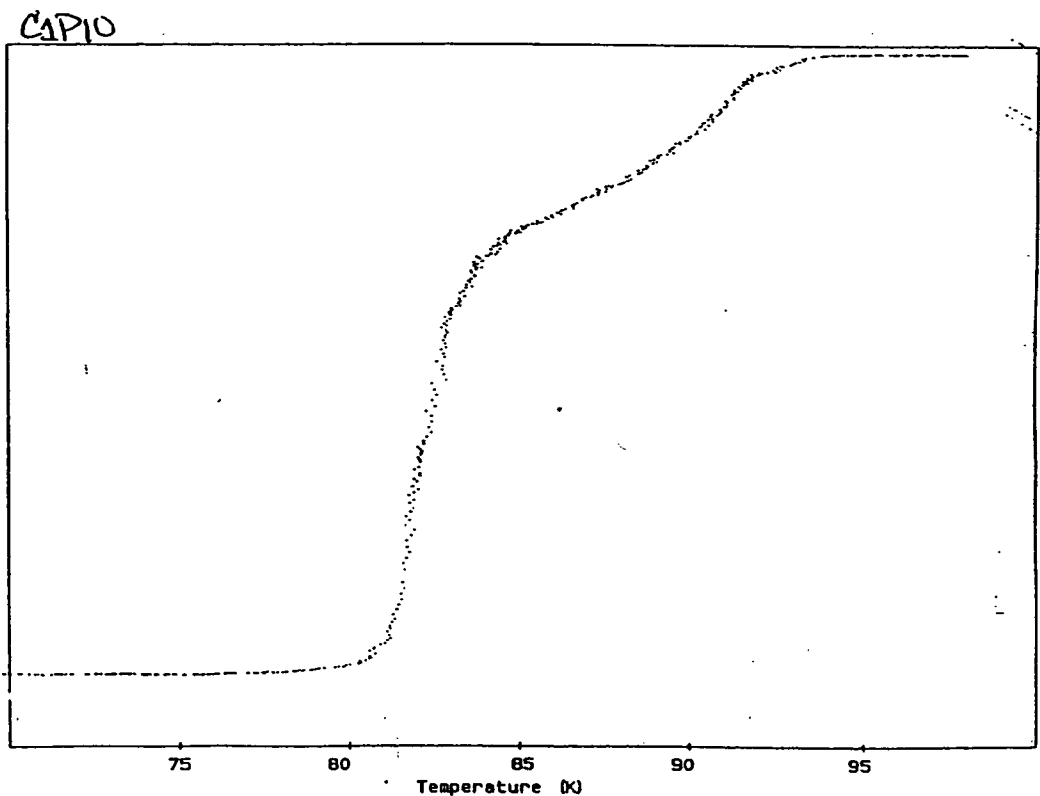
0.17



0.00

$\Delta I$

-0.17



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14 C2 Batch  $\rightarrow \frac{1}{2} \text{Ba}_2\text{Cu}_3\text{O}_7$  200g

From C1 batch calc. (pg. 54 Book III)  $\rightarrow$  72 Book II

$\frac{1}{2} \text{O}_3 \Rightarrow 17.1535 \Rightarrow 17.1707 \Rightarrow \times 2 \Rightarrow \text{34.34}$

$\text{BaCO}_3 \Rightarrow 46.5934 \quad 100 \Rightarrow \times 2 \quad 93.1868$

$\text{BaCO}_3 \text{ conversion: } 93.1868 \frac{197.35}{153.34} = 119.932(3) \div 0.99 \Rightarrow 121.14(4)$

$\text{CuO} \Rightarrow 36.25(81) \Rightarrow 36.2893(4) \Rightarrow \times 2 \Rightarrow 72.57(9)$

O.K. everything is Ba rich by analysis, so why not not correct  $\rightarrow 119.93$   
Apply  $\frac{1}{2}$ .

tare:  $\frac{279.67}{+ 120.54} = 400.21$  won't read, but will tare

reads:  $120.57(4-6)$  was  $\frac{4}{5}$

tare:  $\frac{0.8717}{72.58} = 0.012$   $\text{CuO}$  transfered quant. tare to zero w/ paper

reads:  $\frac{34.34}{5} = 6.868$   $\frac{1}{2} \frac{1}{3}$  transfered quant  
paper weighs 0.1 after checked due to static glove charge, but after glove/charge removal 0.00. Think OK since cal. w/ paper glove while (not more than 0.3% error)  
Expected }  $227.46 \text{ g dry}$   
tot right }

$\text{BaO} - 5.72 \text{ g/c}$   $\text{BaCO}_3 - 4.43$   $\frac{1}{2} \text{O}_3 - 3.01$   $\text{CuO} - 6.3 - 6.49$

$\therefore$  if bumping occurs w/ selective loss,  $\text{BaCO}_3$  should preferentially be lost ~~if~~ not ~~well~~ uniformly suspended.

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Except for 1 bump (0.06 g recovered)  $\Rightarrow$  very smooth, uneventful preparation. Placed in drying oven for weekend drying. (oven cleaned before use also)

12/21 After breaking up coke and re-baking under vac @ 70C for 3 hrs.

~~CRUX~~ #1 transmetal

ideally want 75 per crux

166.67  $\rightarrow$  0.97  
tare  $\frac{86.21}{80.46}$   
-0.01 g recovery

Totals  
80.46  
77.74  
68.29

226.49 expected 227.46 (99.57%)

0.3 g recovered on ~~brushing~~ brushing bke.

CRUX 2  $\frac{172.72}{94.98}$   
77.74  
+0.03 "recovery"

$\frac{226.79}{227.46}$  total 99.7%

CRUX 3  $\frac{173.46}{105.17}$  "white"  
68.29

Rxn. Run 1  $\Rightarrow$  w/ ~~one~~ one 320 ramp to 940C, 450 cool ramp  
14 hrs + 3 up + 2 down = 20 hrs total

12/22 " "

{12/21}

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12/17-18 CENTORR  $SiTiO_3$  RUN

2:00-1700 psi Air usage 16 hr soak @ 1800 w/  $\Delta 500$  psi  
Running Si-Cherty RUN Prog. 05

So for 12/21  $\rightarrow$   $\otimes$   $SiTiO_3$  RUN 24 hrs  $\Rightarrow$  1000 psi  
16  
40 hrs  $\Rightarrow$  1500 psi max permissible

Set for 36  $\Rightarrow$  Ramp started @ 4:25 p.m. 12/21  
3 hrs to temp  
4:25  
36 hours soak  
40:25

1600 psi @ 300C ramp up. 4.25  
44.5 hours total should be O.K

(3 hrs  $\Rightarrow$  1000)  $\Rightarrow$  15,000 projected usage.

12/22 9:00 AM

19.3 soak hours left  $\therefore$   $\Delta t \Rightarrow 16.7 + 3 \Rightarrow 19.7$   $\{ (16 - 11250) \text{ psi} \Rightarrow 4750$

$\therefore$  241.1 psi/hr.  $19.3 + 4.25 = 23.55$   $(241.1 \text{ psi/hr}) = 5,680$

$11250 - 5680 =$  remainder of 5,572 psi } could run longer if rate  
remains constant

6:00 PM

$11,250 - 9,000 \Rightarrow 2,250 / (16.7 - 10.2) = 2250 / 6.5 = 346.2$  !

$346.2 (10.2 + 4.25) = 65,000 \text{ psi} + (9000) = 4,000 \text{ to spare} \checkmark$

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12-22

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C2 RXN seems good, NO APPARENT LIQUID, LARGE SHRINKAGE  
NO VISIBLE GREEN, GOOD BLACK COLOR, BEFORE UNLOADING.

~~Post weight.~~

CRUX #1  
initial

166.97  
86.21  
80.76

100%  
EXPECTED RXN weight.

loss calc.

227.46 theoretical powder

$$80.76 + (80.76 \times (-0.1182)) = 71.214$$

$$\frac{120.54}{227.46} = 0.52994 \text{ wgt \% } \text{BaCO}_3$$

CRUX #2  
initial

172.72  
94.98  
77.74

$$\frac{153.34}{197.35} (0.52994) = 0.41176$$

as above

$$= 68.551$$

$$\Delta = 0.52994 - 0.41176 = 0.1182\% \text{ total}$$

↑  
wrong?

CRUX #3

173.46  
105.17  
68.29

as above

$$= \frac{60.218}{199.983} \text{ total}$$

$$\frac{0.997}{0.997} = 200.58 \checkmark \checkmark \text{ OK.}$$

Actual yields - 1A HR RXN @ 940C

CRUX #2  
2.27g wght  
loss

170.45  
~~94.98~~  
75.47

total wght  
initial time

75.47

ABOVE EXPECTED  
WG HT.

% RXN

6.919  
(9.589)

24.7

CRUX #1  
2.09g wght  
loss

169.92  
86.21  
78.71

78.71

7.496  
(9.546)

21.5

CRUX #3  
1.55g wght  
loss

171.91  
105.17  
66.74

66.74

6.522  
(8.072)

19.2

21.8% } O.K.  
aver?

DATA CONSISTENT

The above understood

and  
no

Date

Date

18 Recheck of wght bxs calc.

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By	137.34	By	137.34
O	15.9994	30s	47.9982
	<u>153.3394</u>		<u>12.0185</u>
	$\sim 153.34$		<u>197.34935</u>
			$\sim 197.35$

$$\frac{153.34}{197.35} = 0.776995 \quad (120.54) = 93.6589999 \quad 126.881 \text{ g}$$

$$26.881 \text{ g} / 3 \text{ cruc.} = \sim 8.96 \text{ g/crucible} \sim \text{correct}$$

Individual wght measures during grinding

12/29

aux 3 66.72 unloaded

105.17	tare
171.82	loaded
<u>171.91</u>	previously
$- 0.09 \text{ g}$	loss = 0.135%
66.74	

169.38
<u>171.82</u>
$- 2.44$
$+ 1.55$
3.99

crux ②

86.20	tare (0.19/20)
78.75	load (-0.02) 78.73
<u>78.69</u>	gain after grinding
$+ 0.06 \text{ g}$	loss $> 0.076 \text{ g}$ loss
<u>164.85</u>	
78.65	0.09 g loss = 0.115% loss

161.68
<u>164.85</u>
$- 3.17$
$+ 2.27$
5.99

total to date

crux ①

75.40/8	unloaded
94.90/8	tare
<u>75.46</u>	load (pre crux)
170.44	loaded
<u>75.46</u>	0.03 loss

167.18
<u>170.44</u>
$- 3.26$
$+ 2.05$
5.31

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Samples were incompletely converted, as right loss indicated. Top was black, but went through a transition of greens progressively over crucible. Ground powder was a dull forest green. Cux 1 slightly darker than 2 & 3. All had white hard agglomerates (presumably  $B_2O_3$ ). Tops indicated oxygen flow throughout crucible. No tops used for second run. Heat treatment.

2/29 New losses consistent w/ cux loading. Conversion now up to 70.8 ~ 71%. Well reground and reweighed initial weighing loss

cux 2  
unloaded 95.02  
ground 72.10

cux 1  
grd. 86.21 ✓  
75.40

cux 3  
grd pot 105.19  
64.15

cux 1 } 192.24 } 188.21 -4.03 22.82 expected 26.807 (85.1%)  
(3 crucibles) 86.24/1

cux 2 } 199.53 } 195.48 -4.05  
95.01

Reground, to 1 crucible

286.00  
86.27

199.73 & 202.47 to start  
(before grd)

$\% (202.47 - 199.73) = 2.74 \text{ g loss } (1.35 \%)$

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Night Loss Summary (by rxn) { crucible }

Crucible #	Initial	Post ①	Post ②	Post ③	Crucible
1	80.76	78.71	75.48	102.0	1 & 3
2	77.74	75.47	72.20	100.47	2
3	68.29	66.74	64.21	202.47	
Thermet	226.79	220.92	211.89		
	227.46				

Final gnd into 1 crucible: pre 202.47  
 gnd post 199.73  
 loss 2.74g (1.35%  $\Rightarrow$  1g spill of saved powder)

Was 85% reacted before this run.  
 Total loss so far slightly less than 2432 g / 27.46 (88.5-85%)

Expect less than, but approx. 3.0 g loss for complete rxn.

0.52994%  $\text{B}_2\text{O}_3$  { (0.77895% of  $\text{B}_2\text{O}_3$  is  $\text{B}_2\text{O}$ ) }

Look for 283 g total upon cooling!

1/5 initial wght. 288.00  
 post 284.17  
 001.83g

199.73 initial  
 197.59 unloaded  
 2.14



1/4  $\text{SrTiO}_3$  synthesis IBM Technical Notebook references book III pgs. 77, A3

21

$\text{TiO}_2$  - 79.8988 g/m

$\text{SrCO}_3$  - 147.6235

$\text{SrTiO}_3$  - 183.5182

$\text{SrO}$  - 103.6194

Ti - 47.90

IN  $\text{SrTiO}_3$  26.1009

Sr - 87.62

IN 47.7446

Take transferred amount to SHAKER JAR ( $\text{SrCO}_3$ ) as basis for  $\text{TiO}_2$  addition

$$\cancel{201.66 \text{ g base}} \frac{48.50}{147.6235} \times 0.32854 \text{ moles} \times 79.8988 \text{ g/TiO}_2 = 26.2499$$

$$= 26.2541$$

~~110.85~~

$$\begin{array}{r} 251.07 \\ 202.56 \\ \hline 48.50 \end{array}$$

$$\begin{array}{r} 251.07 \\ 26.25 / 999 = 26.2763 \\ \hline 277.32 \text{ target } 277.35 \end{array}$$

actual 277.35/6

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and witnessed by

Date

and  
by

Date

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COMPS SCRIPT A1 dated 87/12/02 14:32:25 ..... Page 1

Date: 2 December 1987, 13:24:31 EST  
 From: PLECHAT at YKIVMZ  
 To: PRD

The laboratory results on your samples are:

# C1	Y	Ba	Cu O	Cu=1, ICP
	0.03	0.68	X	
# C2	Y	...	78.1 % (V/V)	
# C3	Ba	...	88.9 %	
# C4	Ti	...	57.3 %	/ error due to static electr. during weighing of sample/
# C5	Ti	...	22.2 %	
	Sr	...	49.4 %	
# C6	Ti	...	24.2 %	
	Sr	...	50.6 %	
# C7	Y	Ba	Cu O	Cu=1
	0.34	0.71	X	
# C8	Y	Ba	Cu O	
	0.34	0.71	X	
# C9	Y	Ba	Cu O	
	2.37	1.10	X	

KMP

Date: 21 October 1987, 10:45:18 EDT  
 From: PLECHAT at YKIVMZ  
 To: PRD

The laboratory results on your samples are:

# C1	Y	Ba	Cu O	Cu=1, ICP
	0.35	0.72	X	
# C1f	Y	Ba	Cu O	
	0.33	0.70	X	
# C5	Y	Ba	Cu O	
	2.21	1.06	X	

Other results to follow from Olson,

KMP

Note: I have produced a light green compound from 123 with  
 the formula: Y Ba Cu O. If interested get in touch  
 12 3 X  
 with me.

*threshold*  
*T<sub>i</sub> consistently low 26e1*  
*Sr consistently high 47.7*

The above understood  
 and witnessed by

Date

and  
 by

Date

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2:

41  
21  
28.17  
tare 86.61  
196.56

initial 197.59  
196.36

1.03 g lost during grinding

Post  
196.56  
194.16  
-2.40

Lost another 2.4 g.. Must be totally converted @ Ruopant.

UNiaxial - 7,000 / 0.371 = 18,870 PSI

0.126 0.611 2.53 4.19 65.8  
0.320 1.55 0.604

C2P1 green  
no final dxs. 2d

C2P2 → Will leave notes on pusher later, too busy. Still see 110. on crucible however, disheartening.

→ 1 mill 4.2 um PSD 10-1 ~ flat dist.

green 27 isopressed

3.59 0.580 0.194 4.274 67.1% (high vs C1)  
1.473 0.493 0.84

C2P3- mill 2 2.53 um ave., much better behaved pellet

(Green)

3.55 0.576 0.210 3.96 62.2% (good agreement w/ C1)  
1.463 0.533 0.896

C2P2- removed @ 600°C ⇒ 20° up to 800, 10° to 975, 20° down

3.59 0.554 0.186 4.89 76.8% ! terrible  
1.407 0.472 0.734 slightly higher than pellet attention

1/13

C2P3 3.57 0.517 0.185 5.57  
1.313 0.47 0.636

87.4%

~ 88

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24 1/13

C2P4 3,775 uni/26,000 1sc

988 1 transient 996 peak  
 2HRS/600 over

3.50/1

0.576 0.206  
 1.463 0.523

3.987 62.6% consistent

1/14

3.49

0.515 0.180  
 1.308 0.457

0.614 5.68 89.2

C2P5

3775/24

990

3.18

0.577 0.199  
 1.466 0.505

0.85 3.74 58.7%

3.15

0.496 0.168  
 1.26 0.427

0.532 5.92 92.9

pellet has stress cracking and photo microstructure with  
 large grain interior and peripheral eggshell of small grains.

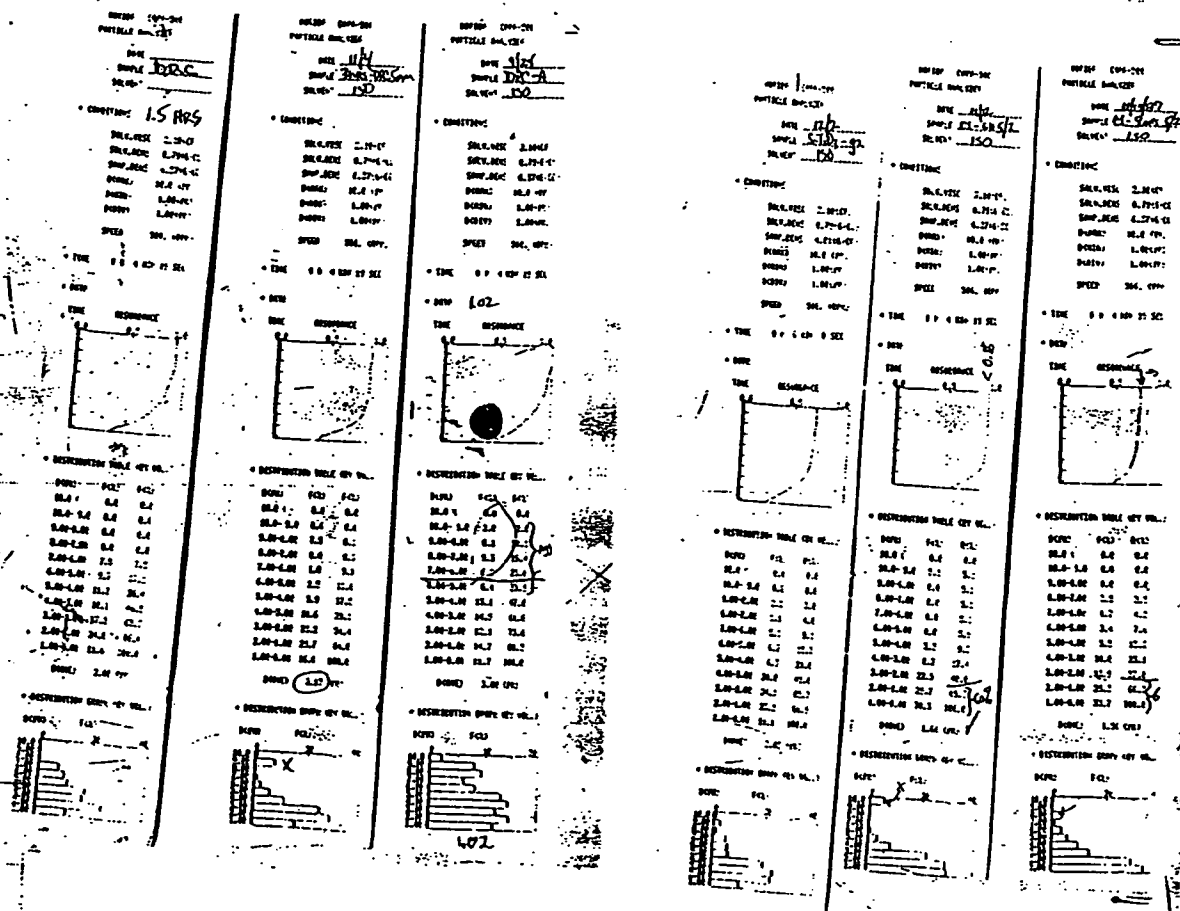
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and  
 by

Date





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**Date**

and  
by

**Debt**

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## 2.

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28 1/19 (18, 17, 16, 15 26th Aug)

IBM Technical Notebook

NOTE → C1 powder

C1 P12, 13, 14, 15 3775/26, 5

C1 P12

3.04	0.574	0.178	3.92	61.5%
3.01	1.478	0.452	0.7755	
	0.506	0.153	5.966	93.66%
	1.285	0.389	0.509(5)	

C1 P13

3.00	0.574	0.175	3.93(4)	61.8%
2.97	1.478	0.444(6)	0.7626	
	0.506	0.150	6.01	94.35
	1.285	0.381	0.494	

C1 P14 (\*)

2.89	0.574	0.169	3.92(7)	61.6%
	1.478	0.429	0.736	

C1 P15 (\*)

3.05	0.575	0.129	4.00	62.8%
	1.460(6)	0.455	0.762(6)	

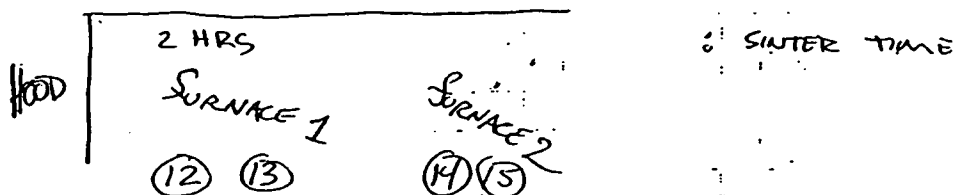
(\*) NO DATA on final pellets - Tom took



IBM Technical Notebook

29

1/19 RUNS IN FURNACE as: all ramps 10°C/min



1/19 A.M. ↓  
4:10 P.M. 4:25 P.M.  
to temp (97.5°C)  
6:10 P.M.  
Ramp down to 600°C soak  
1/20 1:19 P.M.  
Ramp down to RT  
check 2:22 (270°C)

Pellet thickness experiment DD mill powder 3775/26,000

DT2.0

2.04	0.575	0.119		4.03	63.3%
2.01	1.460(5)	0.302	0.506		
	0.507	0.100		6.09	
	1.288	0.234	0.33		95.6

DT1.5

1.54	0.575	0.090		4.01	62.95%
1.51	1.460(5)	0.229	0.384		
	0.509	0.075		6.04	94.8
	1.293	0.190(5)	0.250		

DT1.0K

1.09	0.575	0.065		3.95	62.0%
	1.460(5)	0.165	0.276		

30

IBM Technical Notebook

Cutting Calculations for C1P12, B

$$\begin{array}{r}
 0.108 \\
 0.06 \\
 \hline
 0.048/3 = 0.016
 \end{array}
 \quad 3 \text{ blade thickness} + 0.05$$

C1P12 (0.025) 5 = 0.125  
 (0.025) 6 = 0.150  $\neq$  O.K. from micrometer

use 2 cuts { no 'parallelism' }

$$\begin{array}{r}
 0.050 \\
 0.040 \\
 \hline
 0.11/3 = 0.037 + 0.015 = 0.052
 \end{array}$$

no from edge

1 cut made, BUT PELLET HAS CRACK

$$\begin{array}{r}
 (0.025) 6 = 0.150 \\
 0.040 \\
 \hline
 0.11/3 = 0.037 + 0.015 = 0.052
 \end{array}$$

1/21

DT 1.751 in furnace/no green data (5°C ramp to try to eliminate sinter-cracking)

DT 1.75(2)

1.88	0.575	0.111	3.98	62.5	never run
	1.465	0.282	0.472		

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Date \_\_\_\_\_

IBM Technical Notebook

31

Stereopycnometer

1/27/88

{25/26 supply, miller repair}

28  
29, 2/01

See sheets

Data Points (Multiples)

"83"	$D_A$ 82.95	DRC, DDP12	$D_p$ 95.8
"86"	86.4	JP262, C1P3, C1P2	92.2
"89"	89.3	C1P1, C1P4, C1P7	89.56
"91"	91.3	C1P1, C1P5, C1P8	91.9

note pack: 99.3-95.8

$\Delta 86.4 - 89.3 = \Delta 3\%$

Single Point trends <sup>⊗</sup>

87.5	87.5	JP1	83	seems to NOT clear, <del>could</del> be closed
77		C2P2	95.4	DEFINITELY wide open
"93"	93	DDP13	86.6	indicates closure

⊗ small volumes yield low D values for closed porosity.

32

3500/26,000

IBM Technical Notebook

2/02 Saturday: Porosity Inquiry C1 & C2 @ 975  
 { 10°/min ramp from RT, 2 HOUR SOAK, 10°/min to RT no  
 O<sub>2</sub> equilibration. In order from left to right in rows,

C1P16

3.03	0.575	0.178		4.00	62.8	} <u>GOOD</u> polished
	1.460(5)	0.452	0.757			
3.00	0.500	0.152		5.92	92.9	
	1.293	0.386	0.507			

C1P17

3.26	0.575	0.191		4.01	62.9(5)	} <u>GOOD</u> N
	1.460(5)	0.485	0.812(5)			
3.22	0.508	0.164		5.94	92.8	
	1.290	0.4166	0.544(5)			

C2P6

	0.575	0.192		3.82(6)	60.0	} <u>GOOD</u> N
3.16	1.460(5)	0.493	0.826			
3.11	0.497	0.160		6.12	96.1	
	1.262	0.406	0.507(8)			

C2P7 <sup>chip</sup>

	0.575	0.199		3.79	59.5	} <u>GOOD</u> N	polished
3.21	1.460(5)	0.505(5)	0.847				
3.16	0.497	0.164		6.065	95.2		
	1.262	0.4166	0.521				

C2P7 good & dense, but exterior cracking due to oxygen penetration.  
 Will quench cool by opening furnace. Quench.

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 by \_\_\_\_\_

Date \_\_\_\_\_

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33

ITEM

C2-8 3.08 0.573 0.191 3.82  
1.155 0.485 0.806  
3.06(5) 0.529 0.158 5.53  
1.328 0.399 0.553

59.97  $\Rightarrow$  ~60%  
comparable to previous  
see  
86.8

C1-18 3.07 0.578 0.178 4.01  
1.468 0.452 0.765  
3.03 0.497 0.158 6.04  
1.267 0.401 0.5016

62.95 ~ 63%  
comparable to previous  
94.8

2/12

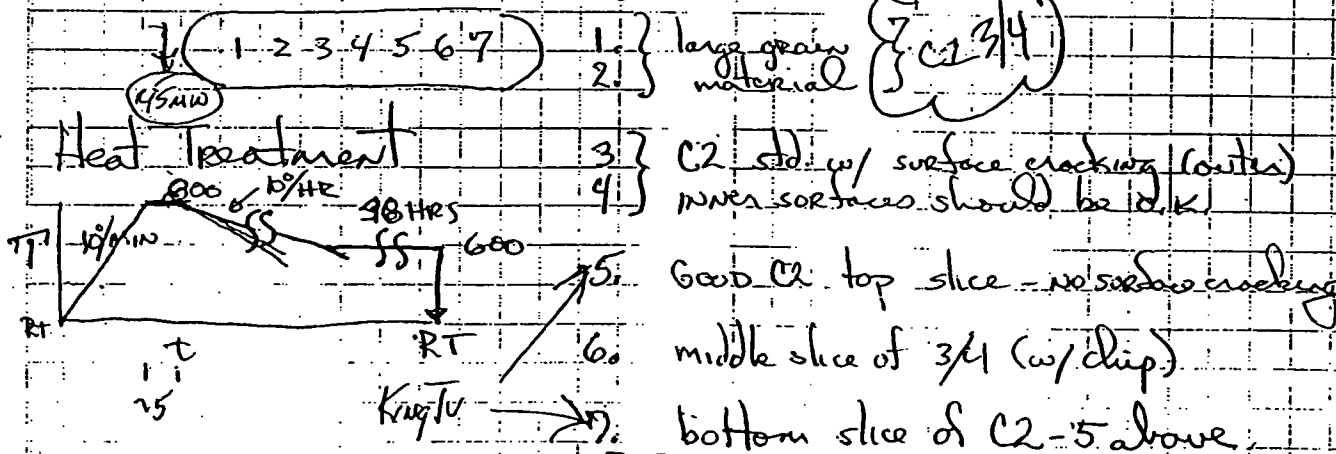
HP-4 green 5,000/27,000

13.98 0.947 ~0.301 4.02(5) 63.2  
2.405 0.764(5) 3.473

Cling C2-8 dry  
ST 0.50

Boat Spots  $\rightarrow$  positioning I.D.

2/15



START: 4:50 PM 2/12  $\rightarrow$  6:15 short ramp down 20 HRS to soak point  
QUENCH 2:50 2/15  $\rightarrow$  3:00 ~ 30 HRS

IBM Technical Notebook

34 2/17 3500/26750

C2-9	3.09	0.575	0.193		3.76	59.0%
		1.460(5)	0.490	0.821		
	3.06	0.510	0.168			85.5 !
		1.295	0.427	0.562		

C2-10	3.06	0.575	0.191		3.77	59.2%
		1.460(5)	0.485	0.812(5)		
	3.02(5)	0.501	0.164		5.77	<del>90.6</del>
	3	1.272(5)	0.417	0.530		89.6

Furnace Oz purge > 1 HR @ 29<sup>(32)</sup> 12:10 P.M. ∴ 945/10 =  
 94.5 mins / 60 min / HR = 1.575 HRS OR 1 hr 34.5 mins (1:45 START  
 1:45-2:15 (1/2 hr sinter) w/ quartz. SINTER)

C2-11	3.02	0.575	0.188		3.775	59.3% O.K.
		1.460(5)	0.477(5)	0.80		
	2.98	0.505	0.159		5.71	89.64 ~90
		1.283	0.404	0.522		

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NOTICE CAPP-546  
PARTICLE ANALYZER

DATE 2/18  
SAMPLE C2-III OT  
SOLVENT 150

D > 0.83

• CONDITIONS

SOLV. FISC 2.16 (CP)  
SOLV. PERS 0.79 (CC)  
SAMP. PERS 6.37 (G/CC)  
D (MAX) 16.6 (PC)  
D (MIN) 1.00 (PC)  
D (DTC) 1.00 (PC)  
SPEED 500 (RPM)

• TIME 0.6 4 RIN IS SEC

• DATE

TIME DISORGANCE

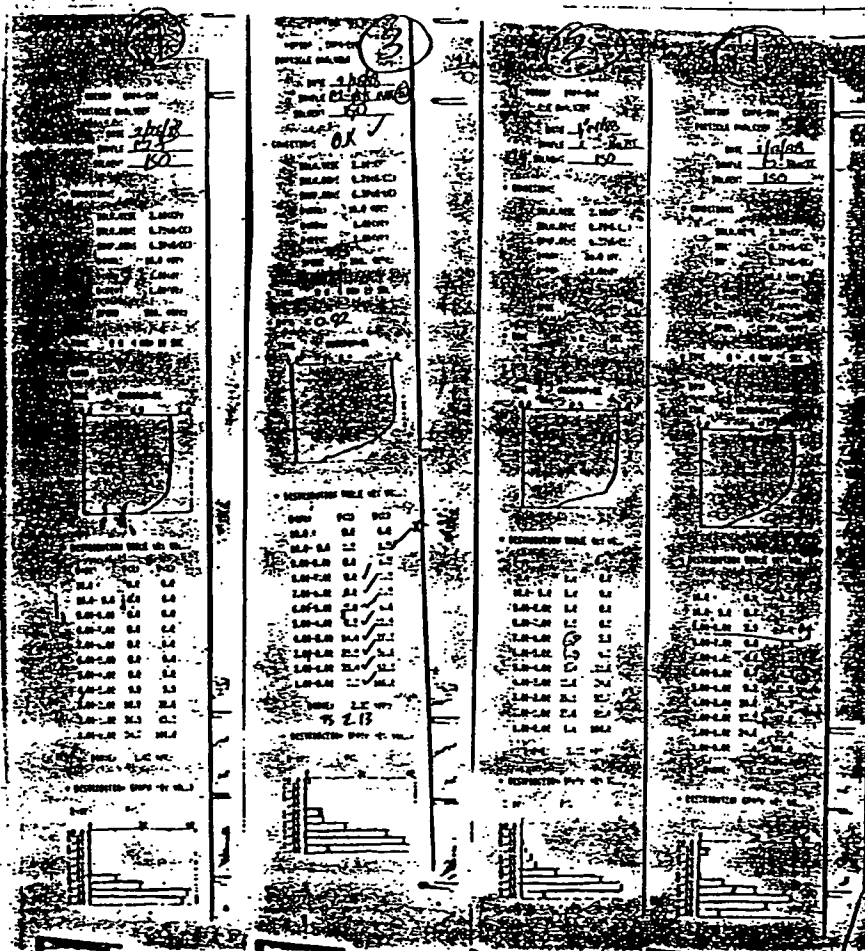
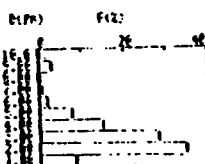


• DISTRIBUTION TABLE (BY VOL.)

D (PC)	F (C)	F (C)
10.0 - 5.0	0.0	0.0
9.00-8.00	2.0	2.0
8.00-7.00	0.2	3.2
7.00-6.00	0.7	3.9
6.00-5.00	1.0	5.7
5.00-4.00	7.0	13.5
4.00-3.00	15.1	26.6
3.00-2.00	26.2	56.8
2.00-1.00	34.7	91.5
1.00-0.00	6.2	100.0

D (C): 2.24 (PC)

• DISTRIBUTION GRAPH (BY VOL.)



C2 PSDS

- 1) C2 MILL PASS II
- 2) C2 + PASS III of 1/2 of ①
- 3) C2 MILL PASS IV of other 1/2 of ①
- ④ fines from ①, ②, ③ III

⑤ 3<sup>rd</sup> MILLING WAS ineffective due to clogged bag  
& powder charged channels

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36  $\text{SrTiO}_3$  3/4 Synthesis (see Book III page 77 for work-up) IBM Technical Notebook

Prep:

$\text{SrCO}_3$	tare 206.15	
	50.00 g	desired
	256.15	
	256.15/6	actual wght
	0.0	$\Delta$
$\text{TiO}_2$	27.062	desired
	283.212	desired
	283.22	actual wght
	+0.01	$\Delta$
	+0.01	scale replace
	$\sim 0.0$	$\Delta$ net

1 hr + mixing

Transfer

tare	89.20	
	166.23	final wght
	77.03 <sup>+</sup>	
	77.062	expected
	-0.03 g	$\Delta$ 0.04

185.56 total prelim wght of top  
 19.33 g top

theoretical expected 151.36 w/out top  
 19.33  
 170.69 w top

3/5

$14.87 + 62.16 = 77.03 \sim \text{correct}$

Ramp @ 700C/hr to 1450C  $\Rightarrow$  to temp  $\sim 3:25$

$0.39/150.97$  (0.258% loss)

GROUND yld  $\Rightarrow 61.39/62.16 \Rightarrow 98.8\%$   
 $\sim 1\%$  grinding loss

Clean X-RAY. MOL. 1 HOUR

Syn PROJECT COMPLETE 3/5

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3/4/88

C2 pellets

C2P12-15  
C2P16-17

IBM Technical Notebook  
1 III  
2 IV

3700/27000

37

C2P12 3.075  
3/21 → (3.08)  
page 44

0.572 0.191  
1.453 0.485 0.804

3.825 60.0

C2P13 3.02  
3/21 → (3.02)  
page 44

0.573 0.188  
1.455 0.477(5) 0.794

3.803(5) 59.7

C2P14 3.11  
page 47

0.574 0.192(3)  
1.458 0.488 0.815

3.82 59.9

C2P15 3.11  
page 49

0.574(5) 0.192(3)  
1.459 0.488 0.816

59.8

C2P<sup>2</sup>16 3.25

0.573 0.202  
1.455 0.513 0.853

59.8

C2P<sup>2</sup>17 3.22 → add 0.02  
SR clipped (3.24) calc

0.573 0.202  
1.455 0.513 0.853

59.6<sup>+</sup>

38  $\text{SrTiO}_3$  GB Doping IBM Technical Notebook

10g  $\text{SrTiO}_3$  w/ 2 wt %  $\text{B}_2\text{O}_3$  added

Sp. g - 8.8 m.p.  $820^\circ\text{C}$

10g + 0.2g  $\text{B}_2\text{O}_3 \Rightarrow 10.2$

0.2g  $\text{Ag}_2\text{O}$  7.14g/cc Decomposes above  $300^\circ\text{C}$

$\text{AgNO}_3 \Rightarrow$  mp  $212^\circ\text{C}$  bp  $>$  decomp 169.8749 mw

4.388g/cc

0.2g  $\text{Ag}_2\text{O} \times \Rightarrow 231.7394$

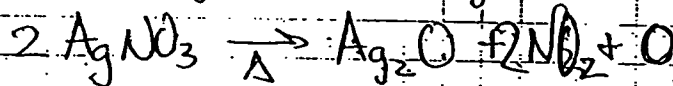
169.8749g  $\text{AgNO}_3$   
g/mw

$\Rightarrow 0.733, 1.364$

0.2g  $\text{Ag}_2\text{O} \times \frac{169.8749 \text{ g } \text{AgNO}_3}{231.7394 \text{ g } \text{Ag}_2\text{O/cc}} = 0.1466 \approx 0.15\text{g}$  OK

$\times 2 = 0.29$

0.2g  $\text{AgNO}_3 \times 169.8749$



~~0.2g  $\text{Ag}_2\text{O} \times \frac{231.7394 \text{ g } \text{Ag}_2\text{O}}{169.8749 \text{ g } \text{AgNO}_3} = 0.274\text{g } \text{AgNO}_3$~~

IBM Technical Notebook

129500 Doped  $SiO_2$  pellets

STA-1 3.10 0.581 0.196  
1.476 0.498  
3.0 0.525 0.178  
1.334 0.452

0.852  
0.632

STA-3 deformed, save points  
3.64 75.7

98.8

STA-2 3.25 0.581 0.208  
1.476 0.521  
3.14 0.525 0.185  
1.334 0.470

0.891  
0.657

3.65 75.9

99.1 ← polish

129

STB-1 3.03 0.587 0.191  
1.491 0.485  
2.88 ← 2.72 (chip) 0.599 0.174  
1.370 0.470

0.847

3.58 74.4

4.47 92.9

STB-2 3.17 0.586 0.197  
1.488 0.500  
3.03 ← 3.21 0.179  
1.370 0.455

0.869(5)  
0.671

3.646 75.9

4.52 94

1295000

STB-3 3.77 0.583 0.237  
1.481 0.60  
3.61 ← 3.74" 0.534 0.216  
1.356 0.549

1.03  
0.793

3.66 76.1

4.55 94.6 ← polish

ST-D1 3.62 0.585 0.235 <sup>varies</sup>  
1.486 0.597  
3.60 ← 3.67" 0.527 0.210  
1.339 0.533

1.03(5)  
0.7505

3.55 72.8

4.77 99.2+ ← polish

Comments - green  $D^k$  fairly consistent, even w/ pressure variation

40

IBM Technical Notebook

DD-X 37/22000  
 2.88 0.573 0.169 4.04 63.4%  
 1.455 0.429 C.713  
 2.83 0.508 0.144  
 1.290 0.366 C.478  
 93

DD-Y 2.99 0.575 0.174 4.04 63.4%  
 1.46(5) 0.442 0.740(5)  
 2.93 0.509 0.149  
 1.293 0.379 C.498  
 92.4

10°C/min RAMP IN NEW  $Al_2O_3$  CRUCIBLE ON FRESH DD POWDR.  
 975°C FOR 2 HOURS { QUENCH. 20min  $O_2$  purge.

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Date and sign every entry. Have entry witnessed. Submit anything possibly new and

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# IBM Technical Notebook

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MODEL CAMP-500  
PARTICLE ANALYZER

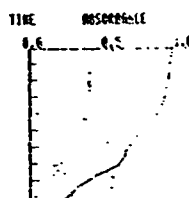
DATE 2/24/88  
SAMPLE 2/24  
SOLVENT ISO

## • CONDITIONS

SOLV. VISC 2.75(CP)  
SOLV. DENS 0.7916(G/CC)  
SAMP. DENS 0.8616(G/CC)  
D(CAR): 10.0 (PP)  
D(CIN): 1.00(PP)  
D(DIN): 1.00(PP)  
SPEED 500. (RPM)

• TIME 0.0 4.0 20 SEC

## • DATA

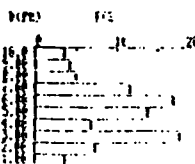


## • DISTRIBUTION TABLE (BY VOL.)

D(PH)	F(C)	R(C)
10.0-9.0	10.0	10.0
9.0-8.0	3.0	12.0
8.0-7.0	4.0	22.0
7.0-6.0	11.0	34.0
6.0-5.0	16.0	50.0
5.0-4.0	12.0	64.0
4.0-3.0	6.0	71.0
3.0-2.0	17.0	85.0
2.0-1.0	7.0	94.0
1.0-0.0	3.0	100.0

D(CAR): 5.00 (PP)

## • DISTRIBUTION GRAPH (BY VOL.)



MODEL CAMP-500  
PARTICLE ANALYZER

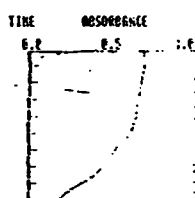
DATE 2/24/88  
SAMPLE 2/24  
SOLVENT ISO

## • CONDITIONS

SOLV. VISC 2.75(CP)  
SOLV. DENS 0.7916(G/CC)  
SAMP. DENS 0.8616(G/CC)  
D(CAR): 10.0 (PP)  
D(CIN): 1.00(PP)  
D(DIN): 1.00(PP)  
SPEED 500. (RPM)

• TIME 0.0 4.0 20 SEC

## • DATA

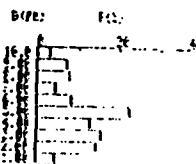


## • DISTRIBUTION TABLE (BY VOL.)

D(PH)	F(C)	R(C)
10.0-9.0	0.0	0.0
9.0-8.0	2.0	2.0
8.0-7.0	7.0	10.0
7.0-6.0	7.0	17.0
6.0-5.0	4.0	22.0
5.0-4.0	0.2	30.0
4.0-3.0	22.0	52.0
3.0-2.0	12.0	65.0
2.0-1.0	15.0	81.0
1.0-0.0	14.0	95.0
0.0-0.0	4.0	100.0

D(CAR): 4.12 (PP)

## • DISTRIBUTION GRAPH (BY VOL.)



MODEL CAMP-500  
PARTICLE ANALYZER

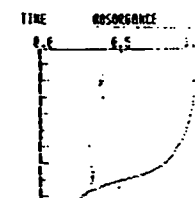
DATE 2/24/88  
SAMPLE 2/24  
SOLVENT ISO

## • CONDITIONS

SOLV. VISC 2.10(CP)  
SOLV. DENS 0.7916(G/CC)  
SAMP. DENS 0.8616(G/CC)  
D(CAR): 10.0 (PP)  
D(CIN): 1.00(PP)  
D(DIN): 1.00(PP)  
SPEED 500. (RPM)

• TIME 0.0 4.0 20 SEC

## • DATA

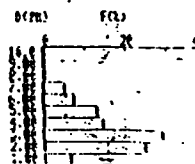


## • DISTRIBUTION TABLE (BY VOL.)

D(PH)	F(C)	R(C)
10.0-9.0	0.0	0.0
9.0-8.0	0.0	0.0
8.0-7.0	0.0	0.0
7.0-6.0	0.0	0.0
6.0-5.0	0.0	0.0
5.0-4.0	12.0	12.0
4.0-3.0	14.0	26.0
3.0-2.0	25.0	51.0
2.0-1.0	24.0	75.0
1.0-0.0	6.0	100.0

D(CAR): 2.45 (PP)

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3/15 DC batch II  $SP_4O_3$

per ton 206.11 (206, unstable  
 $\frac{256.06(7)}{49.95g}$  loss 0.05 (0.1%) desired 50g

$\frac{27.06^2}{283.122}$  target  
 $\frac{283.13}{27.07}$  actual ✓  
 $\frac{17.02}{+0.008}$  total

$\frac{88.34(15)}{17.02}$  Pt. cur. tone  
 $\frac{165.36(7)}{165.34}$  total above  
 expected comb. weight  
 0.03 g error max. ✓ OK. (0.04% error)

~184.54 (19.20 tone) ✓ expect ~154.0 w/out top

~~10.18~~ 150.15 after cooling!

3/16 41.20 < 100 mesh = 59.85 g

ST-D2 3750/25,000  
 (2.9µm) 3.04 0.583 0.206 3.38 70.3 %  
 m.II 1.481 0.523 0.900  
 3.017 0.514 0.181 4.90 1.02 %  
 1.306 0.460 0.616

The above understood and witnessed by \_\_\_\_\_

Date \_\_\_\_\_

and by \_\_\_\_\_

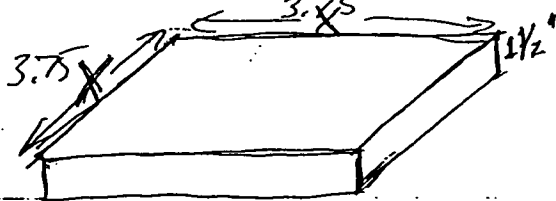
Date \_\_\_\_\_

7070 GLASS count

1 1/2"

70% density -  $2.13 \text{ g/cc} \Rightarrow \frac{\text{kg}}{1000 \text{ g}} \times \frac{0.00571 \text{ lb}}{3.73 \times 10^{-4} \text{ kg}} \frac{\text{lb}}{\text{cc}}$

$0.00571 \frac{\text{lb}}{\text{cc}} \times \frac{16.387 \text{ cc}}{3.75 \text{ in}^3} = 0.0936 \frac{\text{lb}}{\text{in}^3}$  Troy conv.



$4.08 \times 4.08 \times 1.5 = 21.32 \text{ in}^3$

$\frac{21.32 \text{ in}^3}{24.9696} \times \frac{0.0936 \text{ lb}}{\text{in}^3} = 1.99 \text{ lb}$

$1.5 \times^2 \left( \frac{0.0936 \text{ lb}}{\text{in}^3} \right) = 2$

$1.5 (0.0936 \text{ lb/in}^3) \times^2 = 2 \text{ lb}$

$4.78^2$

$0.209 \times^2 = 2 \text{ lb}$

$\times^2 = 18.86$

$\times = 3.77 \text{ in}$

check density conversion:  $2.13 \frac{\text{kg}}{\text{cc}} \times \frac{1 \text{ lb}}{3.73 \times 10^{-4} \text{ kg}} =$

OK

$\frac{0.00213 \text{ kg}}{\text{cc}} \times \frac{1 \text{ lb}}{0.4535 \text{ kg}} = 0.0048965 \frac{\text{lb}}{\text{cc}}$

$1 \text{ lb} = 4.535 \times 10^{-4} \text{ kg}$   
 $1 \text{ lb} = 0.4535 \text{ kg}$

$0.0048965 \frac{\text{lb}}{\text{cc}} \times \frac{16.387 \text{ cc}}{\text{in}^3} = 0.08 \frac{\text{lb}}{\text{in}^3}$

4x4x1.5 or 5x5x1

@ 1" thick  $0.08 \times^2 = 2$   
 $\times^2 = 25$   
 $\times = 5$

44

IBM Technical Notebook

3/21 1<sup>st</sup> pellet 700C for 12 hrs.  $\Rightarrow$  START @ 3 to RAMP @  
 10°/MIN to 800C for 16-17 hrs.

C2P12 for green data on all pellets see pg 37

C2PB 2<sup>nd</sup> pellet 750C to run concurrently

Peter,

Since we didn't get to discuss this experiment in more detail, here is what needs to happen.

5 pellets - C2  
 1st) - 700° C ~12 hr O<sub>2</sub> 308  
 2nd) - 750° C ~12 hr O<sub>2</sub> 302  
 3rd) - 800° C " " "  
 4th) - 850° C " " "

After three intermediate temperature anneal,  
 weigh and measure each pellet. If no sintering,  
 or at least a negligible amount, has occurred, then  
 re-fire each sample for 12 hrs again at the same  
 intermediate temperature and then sinter each pellet  
 for 2 hrs at 950° C. Ramp from the intermediate  
 T to 950° fast (~20°C/min).

Also sinter the 5<sup>th</sup> pellet at 950° C  
 for 2 hrs, this is the control pellet. Thanks  
 and have a good week.

Puane

965C used

3/23 Temp raised to 965C @ 9:00  
 to temp @ 9:15 am

C2P12 3.06 ( $\Delta$ -0.02)  
 3.01

0.572 0.191 no sintering, but 0.65% weight loss  
 0.50 0.163 5.65 88.7  
 1.27 0.414 0.533 CRACKING = closing

C2P13 3.01 (0.05) ( $\Delta$ -0.04)  
 2.97

0.572 0.187 no sintering, but 0.60% weight loss  
 0.504 0.163 5.57 87.4  
 1.280 0.414 0.533 NO CRACKING = open

The above understood  
 and witnessed by

Date

and by

Date



IBM Technical Notebook

45

3/21  $\text{SiTiO}_3$  DRC-batch 2  $\rightarrow$  fine coll after 3<sup>rd</sup> milling  $\rightarrow$  11g yield  
 after cleaning ~ 2g loss to machine  
 3g loss to blow-out  
 fines  $\rightarrow$  1.34  $\mu\text{m}$  ave  
 medium  $\rightarrow$   $\geq$  2.2  $\mu\text{m}$  RANGE (2.2-2.8)  
 approx. expectations { 18% fines  
 82% medium  
 61g / 72 orig.  
 ~ 85% yield

STDX1f-1 0.570 0.212 3.09 64.2% versus 72.3um probe  
 2.74 1.448 0.538(5) 0.887

In furnace ~ 3:00 p.m., tripped off @ 975 2X, cooled to 1400C, then to 1600C.

Temp recovered/reset to 1650 @ 4:30 p.m.

3/22 RAN all NITE! 24 HRS @ 3:00 p.m. Tuesday, 42 HRS @ 9:00 a.m. Weds.  
 2.70 0.487 0.178 4.97 1.033% same as old!  
 1.237 0.452 0.543

Keter.



start section and polish Cu-Bi shot (Start Plan)

start/finish 21/22

Try firing one pellet of  $\text{SiTiO}_3$  to 1350C overnight

Try slip casting a pellet of  $\text{SiTiO}_3$

$\rightarrow$  Finest Jet mill  $\text{SiTiO}_3$  grade down to ~ 1  $\mu\text{m}$ . This will require "fining" the jet mill. Run for 1650C overnight

USED fines, fire 21/2



Mk water bath of  $\text{SiTiO}_3$ ?

tare 202.33  
 00.00  
 252.33 target  
 act weight 252.33  
 27.062  
 279.392  
 act weight 279.4 ~ 0.01

\* approx. due to instability spans down: sometimes stable  
 Transfer. 165.22 act weight

tare 88.17  
 77.05 wght max  
 77.07 expected  
 ~ 0.03% loss

POST/16HR 150.02  
 + 14.87 g expected loss  
 164.89  
 15.2g actual loss

IBM Technical Notebook

46/3/22

C3-Synthesis  
(Reference)

Synthesis  
BaCO<sub>3</sub>

target → 277.72 to zero  
weight: ?

3/23 398.24-6 total  
120.52-54 (-0.02%)

CO

target → 0.89 → zeroed  
weight: 72.58 (7/9) 3/23

transferral grant

CO<sub>2</sub>

target · 0.85 → zeroed 3/23  
weight 34.35

total expected ⇒ 227.46  
transferral grant, +0.03%

Overwrite @ 70C in 30" vacuum after "bump free" isopropyl mixing

3/24 #1 cur 230.56 230.41  
#2 116.57 117.17  
113.99 + 113.24 ⇒ 227.23

0.1% loss or

Prior to removing from bkr after overwrite, cake broken up and "pudged", then let cool under vacuum to remove any sol. resid.

In Surface @ 12:30

POST 219.22  
3/25 102.65  
101.79

218.36

500C/Hr Ramps, 955 RWT in flowing oxygen

218.34  
101.17  
100.94

total  
203.82

202.13

0.83% loss

318.71

The above understood  
and witnessed by

Date

and  
by

Date

3/23 from pg 44 TREATMENT INQUIRY

C2P14 & C2P15 ⇒ original green of info on pg 37; both 3.11 than 1

C2P14: (800°C pretreat), purge - 2120 p.m. 59.9 rd. : 18 HRS  
3.09 0.573 0.191 3.83 60.1 no appreciable sintering  
1.455 0.485 0.806  
3.07 0.522 0.171 5.125 80.5 apparently sintering  
1.326 0.434 0.599 appreciable

C2P15: (850°C pretreat), purge as above - 59.8 rd. : 18 HRS  
3.09 0.565 0.187 4.02 63.1 slight amount of sintering  
1.435 0.475 0.768  
3.08 0.531 0.174 4.87 76.5% initial sintering "appreciable"  
1.319 0.442 0.632

C2P18 (CONTROL) 37/27500  
2.92 0.574 0.180 3.83 60.1% O.K.  
1.458 0.457 0.763  
2.86 0.501 0.152 5.82 91.4  
3/28 1.273 0.386 0.491  
Post 48 hr (2<sup>nd</sup> 2A) - C3 batch

pre → 318.71  
post → 316.88  
(-) 1.83  
202.13  
200.30  
199.23 initial yield

48/23 from page 45 IBM Technical Notebook

STD-1f grain size slightly larger - interior fairly uniform  
 ~ 25  $\mu$ m average occasional

Re-sintered overite to check for additional growth.  
 further polishing of 40 hr sample slice yields numerous 40-50  $\mu$ m  
 GRAINS! Growth seems predictable

3/24

Summary from 45

Base 2.74 1.448 0.538(5) 0.887

3.09 64.2

41.13 @ 2.70 1.237 0.452 0.543

4.97 100.33

1645C

slice back up to 1650 @ 5:00 PM (4 hr earlier due to control couple failure)  
 63 HRS SHUT OFF @ 1:45 PM 3/24 (421 hr)

The above understood  
 and witnessed by \_\_\_\_\_

Date

and

Date

3/24 from pg 45

after additional 12 hr rxn time  $\frac{150.02}{149.81}$   
total loss: 165.22 initial  $\sim 0.21$  g

Assume constant rxn

150.02 16 HR - 15.20 98.6% reacted  
149.81 28 HR - .21 1.4%  
15.41

CASE FOR MINOR porosity?

- > 61 gs recovered after mortar grinding.
- > 2 HRS on shaker mill w/ 5mm balls.
- > 60.4 g shaker yield
- > 48.8 g MI JET YIELD

PSD  
2.91  $\mu$ m ave. Flatter than jet, but not much better  $\phi$  size.

Slip-cast calculations: die 0.9" id.  $\Rightarrow$  2.286 cm  $\frac{0.762 \text{ cm}}{0.3 \text{ " desired green thickness}}$   
 $\frac{\pi \cdot (2.286)^2}{4} (0.762) = 3.1275 \text{ cc } (4.81 \text{ g/cc}) = 15 \text{ g } \text{SrTiO}_3 (0.6 \text{ g}) = 9.0 \text{ g}$   
approx density

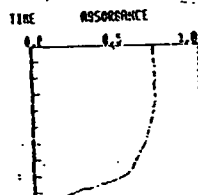
50

IBM Technical Notebook

MODEL CAP-504  
 PARTICLE ANALYZER  
 DATE 3/1/81  
 SAMPLE ST-103-DRC2  
 SOLVENT ISO  
 NAME MIT  
 • CONDITIONS  
 SOLV. VISC. 2.10 (CP)  
 SOLV. DENS. 0.79 (G/CC)  
 SAMP. DENS. 4.81 (G/CC)  
 D(CR2) 16.8 (PH)  
 D(CR10) 1.00 (PH)  
 D(CR15) 1.00 (PH)  
 SPEED 500 (RPM)

• TIME 0 H 6 MIN 0 SEC

• DATA

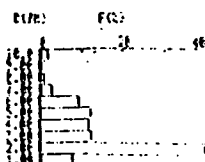


• DISTRIBUTION TABLE (BY VOL.)

D(CP)	F(C)	F(C)
10.0-0.0	0.0	0.0
10.0-9.0	1.0	1.0
9.00-8.00	0.0	1.0
8.00-7.00	1.0	2.0
7.00-6.00	2.0	5.0
6.00-5.00	9.5	15.2
5.00-4.00	12.5	27.1
4.00-3.00	12.1	35.8
3.00-2.00	12.6	52.0
2.00-1.00	35.6	5.1
1.00-0.00	7.9	100.0

D(CR2) 2.20 (PH)

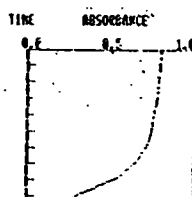
• DISTRIBUTION GRAPH (BY VOL.)



MODEL CAP-504  
 PARTICLE ANALYZER  
 DATE 3/1/81  
 SAMPLE ST-103  
 SOLVENT MIT  
 • CONDITIONS  
 SOLV. VISC. 2.10 (CP)  
 SOLV. DENS. 0.79 (G/CC)  
 SAMP. DENS. 4.81 (G/CC)  
 D(CR2) 16.8 (PH)  
 D(CR10) 1.00 (PH)  
 D(CR15) 1.00 (PH)  
 SPEED 500 (RPM)

• TIME 0 H 6 MIN 0 SEC

• DATA

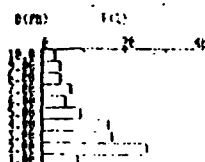


• DISTRIBUTION TABLE (BY VOL.)

D(CP)	F(C)	F(C)
10.0-0.0	0.0	0.0
10.0-9.0	1.1	1.1
9.00-8.00	4.2	7.3
8.00-7.00	4.5	11.5
7.00-6.00	6.9	18.8
6.00-5.00	5.4	24.2
5.00-4.00	9.2	32.4
4.00-3.00	16.6	45.4
3.00-2.00	17.0	61.2
2.00-1.00	25.2	51.6
1.00-0.00	0.4	100.0

D(CR2) 2.20 (PH)

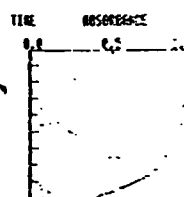
• DISTRIBUTION GRAPH (BY VOL.)



MODEL CAP-504  
 PARTICLE ANALYZER  
 DATE 3/1/81  
 SAMPLE ST-103  
 SOLVENT MIT  
 • CONDITIONS  
 SOLV. VISC. 2.10 (CP)  
 SOLV. DENS. 0.79 (G/CC)  
 SAMP. DENS. 4.81 (G/CC)  
 D(CR2) 16.8 (PH)  
 D(CR10) 1.00 (PH)  
 D(CR15) 1.00 (PH)  
 SPEED 500 (RPM)

• TIME 0 H 6 MIN 0 SEC

• DATA

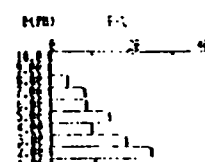


• DISTRIBUTION TABLE (BY VOL.)

D(CP)	F(C)	F(C)
10.0-0.0	0.0	0.0
10.0-9.0	0.0	0.0
9.00-8.00	0.0	0.0
8.00-7.00	4.2	4.2
7.00-6.00	0.4	12.5
6.00-5.00	0.7	21.6
5.00-4.00	10.4	36.2
4.00-3.00	0.5	45.0
3.00-2.00	16.4	64.0
2.00-1.00	24.9	89.0
1.00-0.00	16.7	100.0

D(CR2) 2.20 (PH)

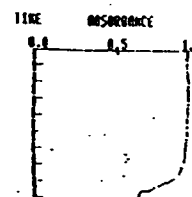
• DISTRIBUTION GRAPH (BY VOL.)



MODEL CAP-504  
 PARTICLE ANALYZER  
 DATE 3/1/81  
 SAMPLE ST-103-DRC2  
 SOLVENT ISO  
 NAME MIT  
 • CONDITIONS  
 SOLV. VISC. 2.10 (CP)  
 SOLV. DENS. 0.79 (G/CC)  
 SAMP. DENS. 4.81 (G/CC)  
 D(CR2) 16.8 (PH)  
 D(CR10) 1.00 (PH)  
 D(CR15) 1.00 (PH)  
 SPEED 500 (RPM)

• TIME 0 H 6 MIN 0 SEC

• DATA

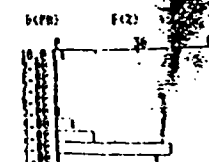


• DISTRIBUTION TABLE (BY VOL.)

D(CP)	F(C)	F(C)
10.0-0.0	0.0	0.0
10.0-9.0	0.0	2.9
9.00-8.00	0.0	2.9
8.00-7.00	0.0	2.9
7.00-6.00	0.0	2.9
6.00-5.00	0.0	2.9
5.00-4.00	0.0	3.0
4.00-3.00	5.9	9.6
3.00-2.00	13.4	23.0
2.00-1.00	43.0	64.0
1.00-0.00	35.9	100.0

D(CR2) 1.34 (PH)

• DISTRIBUTION GRAPH (BY VOL.)



The above understood

Date

and

Date

IBM Technical Notebook

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3/20

10g  $\text{SrCO}_3 \Rightarrow 0.06774$  moles  
5.412g  $\text{TiO}_2$

15.412g total

15.48 after mixing Recovery  
- .27

2/25/93 Note  
Density calculations here  
were done using Pitzer Lit.  
which is now known to be in  
error. It is 5.116 not 4.82

Dave's unreacted  $\text{SrCO}_3/\text{TiO}_2$  { new batch  $\text{SrTiO}_3$  -

8.975 0.584 0.242

2.42 0.458 0.190  
1.16 0.483 0.510

4.745

98.6

NOT TOO GOOD

2.91 0.585 0.194

2.90 0.488 0.173  
1.326 0.439 0.606

4.785

99.5

NOT TOO GOOD

52 A/  $\text{SrTiO}_3$  grow growth IBM Technical Notebook

pellet 2 of fines

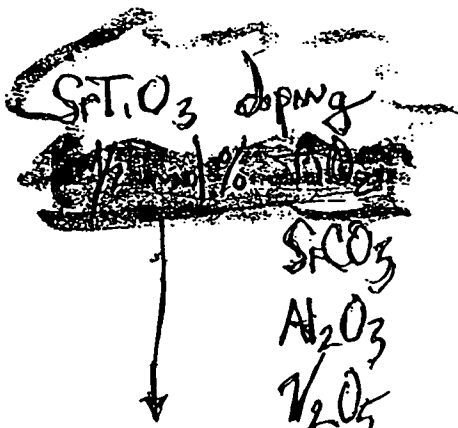
2.22	0.572	0.169	3.12	64.9%	~ same as before
	1.453	0.429	0.711		
2.19	0.487	0.144	4.98	<u>103.5%</u>	= 103.5
	1.237	0.366	0.440		

2.71	0.580	0.176	3.56	74.0%	
Dries excess	1.473	0.447	0.762		
$\text{TiO}_2$					
estimate on 1/2	0.518	0.262	0.160	4.86	<u>\$1.01</u>
etc 35	1.32	0.406	0.556		101.-
(2.70)	<del>1.32</del>	<del>0.406</del>			

~ O.K. by wght.



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0.0676  $\times 2$  0.13525 g batches  
0.125 0.25  
0.036  $\text{as nitrate}$   
0.154 0.308

M.W. 53  
79.90 0.0676  
147.63  
101.96  
181.88 3.337 690C  
183.5182

13.531  $\text{TiO}_2$  moles 0.16935 0.00084675 =  $\frac{1}{2}$  mole %  
25.00  $\text{SrCO}_3$   
38.531

0.00084675 moles (79.90)  $\rightarrow$  0.06766 + 13.531 = 13.46  
0.00084675 (147.63)  $\rightarrow$  0.125 + 25. = 24.875

Summary of additions, quantities

	excess	SUB 1	SUB 2	excess 2
$\text{TiO}_2$ re	13.5986 13.6662	13.443	13.531	13.531
$\text{SrCO}_3$	25.00	25.00	24.875	25.125
$\text{Al}_2\text{O}_3$	—	0.086*	—	—
$\text{V}_2\text{O}_5$	—	—	0.154* 0.16	—

\* these quants are  $\times 2$  since there are 2 moles of Al {  $\text{V}_{1/2}$   $\text{Al}_2\text{O}_3$  }  $\text{V}_2\text{O}_5$

Correction:  $\frac{0.16}{147.63} = 0.00108$  moles  $\text{SrCO}_3$

$\frac{0.00108 \text{ moles}}{0.00169}$  { 64% with loss due to decanting approx  
70% stoic or 30% off addition excess  
 $\text{V}_2\text{O}_5$  }

The above understood and witnessed by

Date

and by

Date

54 4/5

IBM Technical Notebook

Sub2  $\frac{1}{2}O_5$  1 mol % stoichiometric / not excess (see pg 53)

25.0 g  $SrCO_3$  weighed & transferred to beaker

0.16 g removed

0.16 g  $\frac{1}{2}O_5$  added (20cc saturated in hot water, decont)

MISTAKE, now uncorrectable. Should have been:

$0.00084675 \cdot (2) = 0.0016935$  g  $SrCO_3$  removed

$0.0016935 \cdot (147.63) = 0.25$  g however, deconting over

Residual pack reduced actual  $\frac{1}{2}O_5$  addition, and though

NONSTOICHIOMETRIC (slightly) will use to see what happens,

38.62 g red after overnight vac. @ ~90°C

38.53 initial

0.09 loss in mixing

1.3 %

38.88 tare (zeroed)

38.08 406 extra due to final beaker scrape

In furnace to temp by 12:00, 4/6/88 16 HRS 8 A.M 4/7

'Severe' sintering, dark black appearance of pack body

126.96

117.68

$\sim 0.05$  g spillage

117.73

25g  $SrCO_3 \times \frac{103.62}{147.63} \approx 17.55$

126.81

- 117.68

9.28

$\sim 7.40$  g expected loss

26.18

g ground yield

! some bound water?

See 57 & 58  
FOR ENTERED

The above understood and witnessed by

Date

and

Date

Sub 1 ~~Al<sub>2</sub>O<sub>3</sub>~~ → 1 mol % added as nitrate

$$0.00084695(2) = 0.0016935 \text{ moles} // \text{Al(NO}_3)_3 \cdot 9\text{H}_2\text{O} \quad 375.14$$

$\frac{1}{2}$  mol %                      1 mol %                      Al 1:1 so use 0.0016935 moles

$$0.0016935 \text{ moles Al nitrate} \left( \frac{375.14 \text{ g}}{\text{mole}} \right) = 0.6353 \text{ g}$$

(303172)

So remove 0.0016935 moles TiO<sub>2</sub> ∴ 0.0016935(79.9) = 0.135 g TiO<sub>2</sub>

$$13.531 - 0.135 = 13.396 \text{ g TiO}_2, \quad 0.6353 \text{ g Al nitrate in soln}$$

38.29	mix yield
39.03	theoretical
0.74	mix loss

1.9%

$$0.6353 \text{ g} \left( \frac{101.9612}{375.14} \right) = 0.173 - \Delta 0.46$$

$$39.03 - 0.46 = 38.57$$

87.55 tare (removed)  
38.27 note: nitrate decomposes in hot water. Must explain some of loss

In furnace to temp by 12:00 p.m., 4/6/88 ⇒ 16 hrs 8 am 4/7  
little sintering of powder, light SrTiO<sub>3</sub> color, mottled,

$$118.54 - 127.82 = -9.28 \text{ g}$$

same as SUB 2! looking the same, even though exact loss is coincidence.

yield → 27 g

see 57/58  
Sr  
SINTERED  
DATA  
Date

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# IBM Technical Notebook

Two Oxides

119

Figs. 296-301

SrO-SiO<sub>2</sub>

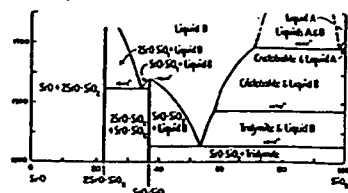


FIG. 296.—System SrO-SiO<sub>2</sub>.

P. Katsube, *Am. J. Sci.*, 5th Ser., 4, 336 (1922); modified by J. W. Geck, *ibid.*, 5th Ser., 13, 19 (1927); see also P. C. Knoch, *J. Am. Chem. Soc.*, 52 (4) 1640 (1930).

ZnO-Al<sub>2</sub>O<sub>3</sub>

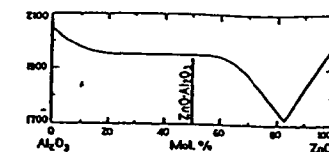


FIG. 299.—Liquidus curve of system ZnO-Al<sub>2</sub>O<sub>3</sub>.

E. M. Bunting, *Bur. Standards J. Research*, 8 [2] 220 (1932); R. F. 412.

SrO-TiO<sub>2</sub>

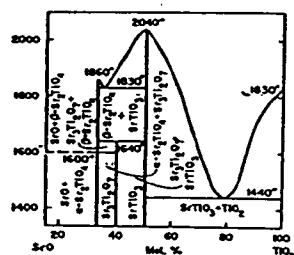


FIG. 297.—System SrO-TiO<sub>2</sub>.

Miroslawa Dryl and Wladyslaw Trachiatowski, *Rachunki Chem.*, 31, 492 (1957).

ZnO-B<sub>2</sub>O<sub>3</sub>

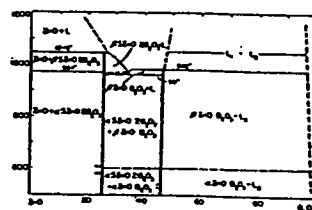


FIG. 300.—System ZnO-B<sub>2</sub>O<sub>3</sub>.

D. E. Harrison and F. A. Hummel, *J. Electrochem. Soc.*, 103 [9] 406 (1956); see also "Structure of Zinc Bismuthate, ZnO(BiO<sub>3</sub>)", F. Smith, S. Garcia-Blanco, and L. Beron, *Anales Real Soc. Espan. Fis. Quim. (Madrid) Ser. A (Nouv. Dec.)*, 263-268 (1961).

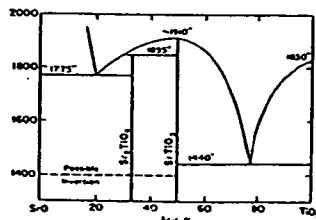


FIG. 298.—System SrO-TiO<sub>2</sub>; tentative.

Rustum Roy; private communication, 1957.

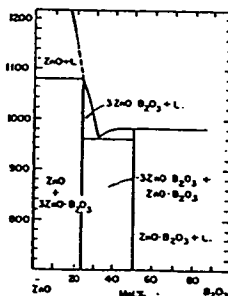


FIG. 301.—System ZnO-B<sub>2</sub>O<sub>3</sub>.

Yu. S. Leonov, *Zhur. Neorg. Khim.*, 3, 1246 (1958).

Two Oxides

93

Figs. 2334-2336

SrO-TiO<sub>2</sub>

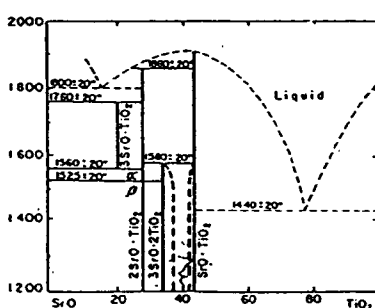


FIG. 2334.—System SrO-TiO<sub>2</sub>. SrO-TiO<sub>2</sub> is extended to approximately the SrO:TiO<sub>2</sub> composition.

Antonio Cocchi and Franco Mazzanti, *Ann. Chim. (Rome)*, 53, 802 (1953).

SrO-ZrO<sub>2</sub>

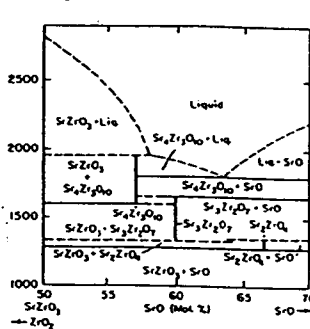


FIG. 2335.—System SrO-ZrO<sub>2</sub>.

Gilbert Tillett and Monique Percey y Jorba, *Rev. Roum. Phys. Chim. Nucl.*, 1 (4) 237 (1954).

These Diagrams (arrows) for SrO-TiO2 system and asserted others

The above understood

Date

and

Date

Excess  $\text{SrTiO}_3$

(Excess 2) IBM Technical Notebook

(Excess 1) ➡

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13.531  $\text{TiO}_2$   
➡ 13.53-

25.25  $\text{SrTiO}_3$   
25.28

13.6  $\text{TiO}_2$   
13.61

25.00 Sr  
25.02  
.03 tlb.

zero off after addition  
probably static

In drying oven @ ~100C under house vacuum @ 1:30 p.m. 4/6/61

38.72 after drying  
87.87 weighed crucible  
126.59 w/ addition  
118.85  
7.74

38.43 after drying  
87.07  
125.50  
117.59  
7.71

$25 \times \frac{101.86}{375.14} = 6.795$  17.5

$\frac{6.795}{7.74} = 88.25\%$  + 12% excess loss  
 $7.5 / 7.7 = 97.5\%$

#1  $\text{TiO}_2$

#2  $\text{SrCO}_3$

NO GREEN DATA TAKEN

➡ NO GREEN DATA

$\text{N}_2$  2.75 0.520 0.159 4.96 1.03  
1.321 0.404 0.554  
2.71 0.529 0.160 4.71 97.9  
1.344 0.406 0.576

3.01 0.517 0.175 5.0 1.04  
EXCHANGE 1.313 0.444(5) 0.60  
3.00 0.520 0.176 4.89 1.02  
1.321 0.447 0.613

SrB2  
2.38 0.540 0.135 4.69 97.5  
1.372 0.343 0.507  
 $\text{N}_2$  2.41 0.554 0.141 4.31 89.6  
1.410 0.358 0.559

SrB1  
2.56 0.529 0.150 4.74 98.1  
1.314 0.381 0.5405  
2.60 0.526 0.151 4.83 1.00  
1.336 0.384 0.538

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SUBSTITUTION 1 :  $Al_2O_3$ , 1 mol % 16 HRS. RUN  
 " 2 :  $Y_2O_3$  ↓  
 N<sub>2</sub> O<sub>2</sub>  
 1 : 100.4 98.5  
 2 : 89.6 97.5

EXCESS DOPING 1 :  $Y_2O_3$  1 mol %  $Ti_2O_3$   
 " 2 :  $SrCO_3$   
 N<sub>2</sub> O<sub>2</sub>  
 1 : 97.4 103  
 2 : 102 109

MECHANICAL MANIPULATION  
 fines : 103.4  
 fines  $1/3$ , med  $2/3$  mix : 102.3  
 MED : 100.4

4/11 Phase Co/Bi studies IBM Technical Notebook

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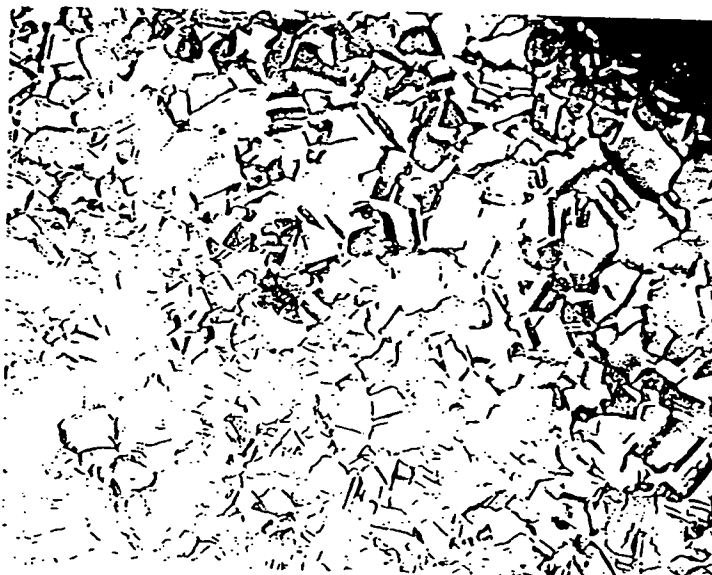
600C overnite  $N_2$  treatment on as rec'd material (Cu)



INTERIOR  
INHOMOGENEOUS  
(ABNORMAL)  
GRAIN GROWTH

100X

100  $\mu$ m



EXTERIOR  
INHOMOGENEOUS

100  $\mu$ m

The above understood  
and witnessed by \_\_\_\_\_

Date \_\_\_\_\_

and  
by \_\_\_\_\_

Date \_\_\_\_\_

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1, 3, 10% Bi in copper

5 g total per batch

4.95 post 750C

$g\text{ Bi} : 5(0.01) = 0.05 \quad 5(0.03) = 0.15 \quad 5(0.10) = 0.5\text{ g}$

Cu	<u>4.95</u>	<u>4.85</u>	<u>4.50</u>
actual	0.05-6	0.15-0.16	0.50-1
	4.95-6	5.00	4.99-5.0
recovery	4.87 added to 5.00	4.99 -	4.95

5.00  
 4.98 after 400C over (not disturbed)      4.90 after 400C overnite

Reloaded 1% & will continue w/ 3%. Will make a new 10% and a 50% and fire @ 750C. Crucible shortage → will likely modify above.

50/50

2.5g Bi, 2.5g Cu

10% Bi

3% as above

g Bi: 2.51 actual

post Cu 5.01

Cu 2.40

crucible total

1.34  
6.34  
 5.00  
~~(4.99)~~

Post 750C

6.3  
 4.91

0.51  
5.02(3) total  
 4.51(2)

1.32(3)  
6.24  
 5.07 ?  
 4.92

Post 750C

6.21  
4.89  
 4.00C RESULT

NOTE: INITIAL 400C (420C) follow (1-10%) percentages of Bi did not produce expected densification/solidification of pucks.



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25% { 35% Bi/Cu melts  $\leq$  1 Bi crucible filling

25%  
 $0.028(5) = 1.25g \text{ Bi}, 3.75g \text{ Cu}$

6.33 PRE  
 $\frac{1.33}{5.00}$

36  
1.75 Bi ; 3.25 Cu

6.25(4) loaded  
 $\frac{1.30(1)}{4.95}$  starting total

6.30 post  $\Delta = 0.03$   
Possible post density: 0.315, 0.385  
4.97 0.800, 0.978 0.6 8.28

6.23  $\Delta = -0.02$

90.  
definitely smaller volume, higher density

Argon/H<sub>2</sub> Bi filling

13.32 post

2.2 PRE

13.18

11.86

0.148

13.30 after slag removal

filled 12.82  
cruc:  $\frac{11.39(46)}{11.43}$

CRUX  $\Rightarrow$

25%  
1.26 Bi  
5.03 w/Cu

post 12.81

ARGON/H<sub>2</sub> 25% Bi Run  $\leftarrow$  Pellet Run  $\rightarrow$

pellet: 4.87 0.485 0.222 7.25 79%  
1.232 0.564 0.672

$8.96 \times 0.75 + 0.25(9.8) =$   
 $6.72 + 2.45 = 9.17$

French started 2HR purge 3:35"  
4.84 0.483 0.234 pellet bloating due to Bi vaporization?

B<sub>12</sub>O<sub>3</sub>: sp. g. 8.8 m.p. 820°C

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$\text{SnTiO}_3$  GRAIN Growth Experiment - MECHANICAL MEASURES

- 1) PSD weighting
- 2) fines full density & free sintering of polished surface
- 3) reacted to constant weight (1st batch) sintering as in #2

FINES = F

2.04	0.570	0.155		3.14	65.3
	1.498	0.394	0.649		
2.01	0.488	0.132		4.975	10.84
	1.239(5)	0.335	0.409		

Fine/medium = FM

2.19	0.577	0.154		3.32	69.0
	1.465	0.391	0.659		
2.17	0.504	0.135		4.92	102.3
	1.28	0.343	0.441		

changed  $\mu$

2.46(7)	0.582	0.165		3.43(5)	71.4
	1.478	0.419	0.719		
2.46*	0.589	0.147		4.85	100.4
	1.318	0.373	0.509		

REMARKS  $\rightarrow$  \* some powder adhered

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4-12-88<sup>63</sup>

# Sintering Regime

Rapid Temp w/ 10 cc/min O<sub>2</sub>

1550C initial set, after REACHING temp for 1 HR, 1640C overnight  
5:20 p.m. ~ 1100C, T<sub>control</sub> blown. @ ~ 30-45 minutes @ 1540.  
Restarted @ ~ 5:55 & brought directly to 1640C.

The above understood  
and witnessed by \_\_\_\_\_

Date \_\_\_\_\_

and  
by \_\_\_\_\_

Date \_\_\_\_\_

644-26-88

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LEAK TESTING - S.C. TORR HIGH VAC

25 millitor after continued pumping through system  
STARTING WITH roughing in

Will check pumpdown through HVAC valve alone  
tomorrow.

4/27 → Vacation

4/28 Pump down through high vac initially unsuccessful, must  
have been stuck valve, but after freeing can get down  
to ~50 millitor in 15 minutes. Will continue pumping.

1/2 40

Down to 10 thru rough, 30 w/ HVAC only,  
Rather quick leak-back when both closed off indicating  
leaks in system:

- 1) FURNACE
- 2) Elbow connection
- 3) Pump

See page 78

5/13 Promised CSS test Monday (Chad!)

5/13

First Milling - AutoSeed - Teflon liner (13

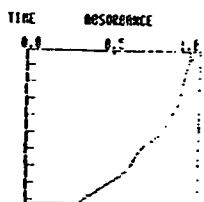
48.17 g known, but "few" oxide before total process night. checks

49.69 g yield

NORIDE CAPR-SEE  
PARTICLE ANALYZER  
DATE 5/13  
SAMPLE C3-Part I  
SOLVENT ISO  
Teflon liner  
• CONDITIONS  
SOLV. VISC 2.10 CCP  
SOLV. DENS 0.7516/CC  
SAMP. DENS 6.3416/CC  
D(CRUX) 10.0 (PH)  
D(CRUX) 1.00 (PH)  
D(CRUX) 1.00 (PH)  
SPEED 500. (PPH)

• TIME 0 H 4 MIN 20 SEC

• DATE

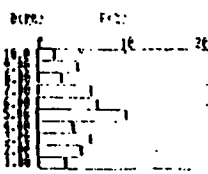


• DISTRIBUTION TABLE (BY VOL.)

D(PH)	F(%)	R(%)
10.0 - 9.0	49.7	49.7
9.00-8.00	1.0	51.6
8.00-7.00	4.5	56.1
7.00-6.00	2.7	58.8
6.00-5.00	6.1	64.9
5.00-4.00	6.9	71.7
4.00-3.00	10.2	81.9
3.00-2.00	4.0	85.9
2.00-1.00	6.0	91.9
1.00-0.00	5.0	96.9
0.00-0.00	3.2	100.0

(AVER) 5.85 (PH)

• DISTRIBUTION GRAPH (BY VOL.)



The above  
and witnessed by

PASS II 5/10

47.6 g yield: much fluffier, looks  
~ like 5um powder.

IMMEDIATELY REMILLING

pg. 66 for PSD sheets ~2g loss

PASS III 45.8  
45.8

PASS IV 44.5  
~ 18.0 5 pellets  
26.5

4 High large particle % 41.7 vs 18 for C2

4 overall ave. ~10 vs 5-6 for C2

however distribution seems similar { some  
bypassing must have occurred.

Will work on Tuesday.

Date

and  
by

Date

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anything a w on y entry. Have every possibly important  
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ssibly new and inventive.

66

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Date

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B<sub>1</sub>/C<sub>0</sub> 25/75 erocible packed, sinter overnite in Ar/H<sub>2</sub>(5)  
@ 750C.

#1 → < 100 mesh Cu, spherical ("new")

#2 → <sup>10μm</sup> ~~100 mesh~~ ~~spherical~~ Cu (old)

#3 → penetration  
10μm spherical

#2: 1.25/5.01  
6.31  
ceux 1.34  
5.00

#1: 1.25/5.00  
6.35  
1.35  
5.00

POST 6.31

6.32

8.0-8.5 mm L

8.37

9.65-9.75 mm dia

9.65-10.0

After interruptions: 5/24/ start cut { polishing  
6/8/88 finish: 6/8/88 after

{ Porosity is reduced, and 3<sup>rd</sup> <sup>(grey)</sup> 'oxide' has been eliminated }  
in forming gas.

The above understood  
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and  
by \_\_\_\_\_

Date \_\_\_\_\_

68 C3- P1-5 Green Data { IBM Technical Notebook } Picked up mill test on  
 150275 G mm mm Material ruined  
 C3P1 3.59 1.470 0.779 0.80 70.5  
3.33  
 C3P2 3.33 1.477 0.442 4.40 69%  
 2.93 0.757  
 C3P3 3.58 1.472 0.478 4.40 69%  
 0.813  
 C3P4 3.37 1.476 0.440  
 C3P5 3.53 1.474 0.471 5.52 87 even w/ cracks  
 3.19! 1.331 0.415 0.577 pick OK. I think  
 Mill no good.

NOTES: PELLETS SEEM TO HAVE SHED ORGANIC/GAS?!  
 looks like the pellet melted in plastic container.  
 15026 UNIC 6200 20% → 550, 10% → 975, 2 HRS,  
 C3P6 2.52 1.50 0.32 4.46 70.1%  
 coarse 2.50 1.482 0.316 0.565 4.55 71%  
 0.55

The above understood  
 and witnessed by

Date

and  
by

Date



Calcinations - 750C IN @ 8:00 P.M. 5/17/88 out 9:00 AM 5/18 69

TiO<sub>2</sub> - Green 3-9's

$$\begin{array}{r} 16.3620 \\ - 0.8610 \\ \hline 15.501 \text{ g TiO}_2 \text{ weighed} \end{array}$$

$$\begin{array}{r} 89.4610 \text{ crux} \\ 105.0174 \text{ crux + TiO}_2 \end{array}$$

15.5564 g TiO<sub>2</sub> by difference

$$\begin{array}{r} \text{s/r Post} \\ 105.0174 \\ \hline 104.9395 \\ 0.0779 \end{array} \text{ gaining } \Delta T > \Delta T_{\text{CO}_2}$$

$$15.501 = 0.5\% +$$

$$\begin{array}{r} \text{EQ} \rightarrow 105.0084 \\ \hline 105.0174 \\ 0.0090 / 0.0779 = 88.5\% \text{ bal} \end{array}$$

$$99.64\% \rightarrow 0.3\% \Delta + 0.0554$$

SrCO<sub>3</sub>

$$\begin{array}{r} 18.4193 \\ 0.8710 \\ \hline 17.5473 \end{array} \rightarrow \begin{array}{r} 0.8732 \\ \hline 17.5441 \end{array}$$

$$\Delta 0.0032 \approx \Delta \Delta D.f !!$$

$$\begin{array}{r} 109.9615 \\ 92.3660 \\ \hline 17.5955 \end{array} \Delta + 0.0514$$

$$\Delta \Delta D.f \Rightarrow 0.004 \text{ g} \sim 4 \text{ mg calibrate}$$

$$\begin{array}{r} \text{Post } 109.9615 \\ 109.8870 \\ \hline 0.0745 \end{array} \text{ gaining } 17.5441 = 0.4\%$$

$$\begin{array}{r} \text{EQ } 109.9510 \\ \hline 109.9615 \\ 0.0105 \end{array} 85.6\% \text{ back}$$

5/19 TiO<sub>2</sub> { ~~SrCO<sub>3</sub>~~ 2<sup>nd</sup> Cal POST

$$\begin{array}{r} 105.0174 \\ 104.8670 \\ \hline 0.15 \end{array} (-0.0003 \text{ cal})$$

$$\sim 1\%$$

$$\begin{array}{r} 109.9615 \\ 109.8580 \\ \hline 0.1035 \end{array} (-0.0003 \text{ cal})$$

$$\sim 0.6\%$$

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HF Silicon Etch/Wash/Buffer Solns.

~~80g~~  $80g \text{ NH}_4\text{F}$  in  $120g \text{ H}_2\text{O}$  (distilled)  $\Rightarrow$   $\sim 120cc$  40 wt. %  $\text{NH}_4\text{F}$  REAGENT

actual soln is 40:1 ~~10:1~~  $\sim 170cc$

BHF  $\rightarrow$  40 parts  $\text{NH}_4\text{F}$  reagent : 1 part HF (49 wt%) soln.

QUENCH  $\rightarrow$  10:1 DI :  $\text{NH}_4\text{OH}$  reagent 50ml:500ml

BHF clean  $\rightarrow$  10:1:2.2 ( $\text{NH}_4\text{F}$  : HF : Glycerin)  
reagent 49

$16(10) = 160$   $16(1) = 16$   $16(2.2) = 35.2 = 211 \text{ ml}$   
320  
350  
(190) (35) (77)

MSG:FROM: SARDESAI--FSHVMCC TO: MDT --YKIVMT  
To: MDT --YKIVMT

05/18/88 12:39:40

From: Viraj Sardesai  
8-533-8545, SCL Pers Metals, GTD E. Fishkill  
IBM INTERNAL USE ONLY (Unless otherwise specified)  
SUBJECT: BHF concentrations used in SCL

Michael,

We use 40:1 BHF for pre platinum, emitter screen ox removal and for s metal pre-clean.

The chemical is commercially available premixed solution and has 40 parts (by volume) of 40 wt pct  $\text{NH}_4\text{F}$  solution mixed with 1 part of 49 wt pct HF solution. Both  $\text{NH}_4\text{F}$  and HF are in aqueous solutions. Manufacturer specs the HF concentration to 0.61 to 0.77 moles per liter and specific gravity of 1.106.

For S postL/O BHF clean 10:1:2.2 ( $\text{NH}_4\text{F}$ :HF:Glycerin) is used prepared similarly and quenched in 10:1  $\text{NH}_4\text{OH}$  solution (28 Wt pct  $\text{NH}_4\text{OH}$  solution diluted to 10 times its volume in DI water).

cc: SZECSY --FSHVMCC

HOUGHTON--FSHVMCC

Regards,  
VIRAJ

FSHVMCC(SARDESAI), D/11G B/322 Z/STI

\*\*\*\*\* OUR TEAMWORK MAKES THE DIFFERENCE ! \*\*\*\*\*

BHF concentrations used in SCL

BHF

BHF CLEAN

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and  
by \_\_\_\_\_

Date \_\_\_\_\_

5/18 Polymilling

IBM Technical Notebook - mill #2

73

40g batch yield

I 36.8

II 33.4

III 31.3

IV 28.4

V 25.75

DO

PSD 1 2 Δ

6.94 4.84 3

3.65 3.21 3

3.53

2.98!

3.1!

(2) bag charger required

3 actually higher error 7% @ 7.

2.5 New bag

The above understood and witnessed by \_\_\_\_\_

Date \_\_\_\_\_

and by \_\_\_\_\_

Date \_\_\_\_\_

ISO 28,

74

IBM Technical Notebook

MARGINAL GREEN  
 DENSITIES

C3P6	3.29	1.474	0.971		4.11	64.6
				0.80		
	3.23	1.343	0.416		5.48	<u>86.2</u> !
				0.59		
C3P7	3.19	1.476	0.955		4.00	64.5
				0.779		
	3.13	1.343	0.404		5.49	86.3
				0.57		
C3P8	3.21	1.473	0.962	0.787		64.1
	3.16	1.341	0.409	0.577	5.48	86.2
						} TO KING-TU
C3P9	3.08	1.474	0.441		4.09	64.3
				0.7525		
	3.02	1.336	0.391		5.51	<u>86.6</u>
				0.548		

NOTES: PELLETS W @ 4:55 with flowing O<sub>2</sub> (bottled, dessicated)  
 Heating started @ 5:15 @ 20°/min (97C @ start)  
 @ 265C cut back to 10°/min; to reach sinter T' @ 6:35 p.m.  
 Sintering @ 975C for 2HRS. till 8:35 p.m.  
 Quench } remove.

The above understood  
 and witnessed by \_\_\_\_\_

Date \_\_\_\_\_

and  
 by \_\_\_\_\_

Date \_\_\_\_\_

IBM Technical Notebook

75

995C sister  
CSP10 3.18 1.474 0.453 4.114 64.7  
3.11 1.338 0.399 0.773cc 5.54 87.2  
0.561

no (appreciable) liq.  $\phi$ !

T3 "leg"  
yld 10.35  
PASS  $\Delta$  MILL #1  
Ave. part dia.  
<100 mesh  
29.~ I 10 ! 12g leaks 3.29  
21.5 II 8 ! ~1g leak 3.11  
18.5 III 3 ! 4.0<sup>+</sup> g of ~2.0 $\mu$ m powder in mill neck  
22.4 total max yield

The above understood  
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Date \_\_\_\_\_

and  
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Date \_\_\_\_\_

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Date \_\_\_\_\_



# "T3" pellets IBM Technical Notebook

C3P10-18

9750

C3P10 ①	3.14	1.461	0.473		3.975	62.50
✓ 3.08	1.308	0.400	0.79		5.75	<u>90.4</u>
			0.536			

C3P12 ②	3.28	1.462	0.495			
✓ 3.21	1.308	0.417	0.56	5.73		<u>90.0</u>

C3P12 ③	3.04	1.463	0.450			
2.97	<del>1.308</del>	0.388	<del>0.54</del>	5.68		<del>89.31</del>
	<del>1.310</del>	0.385	0.523	5.756		90.5
	<del>1.306</del>		0.516			

RECHECK TOMORROW

C3P14	3.21	1.464	0.473			
✓ 3.14	1.308	0.405	0.548	5.77-8		<u>90.7-9</u>
	1.306					

10000

C3P15	3.04	1.461	0.458			
2.97	1.298	0.386	0.511	5.81		91.35

C3P16 (pelules)	3.08	1.466	0.457			
3.02	1.301	0.390	0.519	5.82		91.5

C3P17	3.28	1.464	0.492		5.75	<u>90.4</u>
3.22	1.298	0.422	0.568	5.82		91.5
(3.28)						

chip offset

78 6/8/88

IBM Technical Notebook

Centorr HVAC system close to finished with leak testing,  
preliminary operation checks.

System mechanical pump down < 20-30 minutes

Torbo molecular ↓ down → to  $5 \times 10^{-5}$  within 1 hr  
with attachments to mid 6's by 1:00 p.m.  
Start was 9:15 originally.

Block-off flange, new Centorr purge / plug fittings still  
needed. Fouling seal test req'd.

The above understood  
and witnessed by \_\_\_\_\_

Date \_\_\_\_\_

and  
by \_\_\_\_\_

Date \_\_\_\_\_

# Bi/Cu Free-Crucible Sinter Vacuum Run

To glass shop 6/17/88. Batch size to be 4.0 g to allow for ease of manipulation during sealing of quartz tube.

$$4.0 (0.25) = 1.00 \text{ g Bi}$$

$$\downarrow (0.75) = 3.00 \text{ g Cu (will use 10 \mu m Cu powder)}$$

$$\begin{array}{r} \text{Bi} \rightarrow 1.00 (0.99) \\ \text{Cu to } 4.03 \\ \text{Cu } 3.03 \end{array}$$

$$\text{from JAR } 4.02 (1)$$

$$\begin{array}{r} \text{cruc } 1.33 \\ \text{w/ mix } 5.33 (4) \\ 4.00 (1) \\ \hline 4.04 \end{array}$$

$$\begin{array}{r} \sim 24.8\% \quad \sim 25 \\ 75.2\% \quad 75 \end{array}$$

Pero - spilled in glass shop

6/9 New crucible shape/size for stability

lets take 5.0 g batch

$$1.25/5.0 (\pm 0.01)$$

$$\begin{array}{r} \text{crucible } 3.35 \\ \text{w/ mix } 8.35 \\ \hline 5.00 \end{array}$$

6/14 After overnite sinter & removal from quartz tube

cruc. & sinter 8.30g (some spillage w/ tube before heat treatment)

no appreciable vapor product seen

CONCLUSIONS: Vacuum doesn't appear to work as well as Ar/H<sub>2</sub>. Sample full of holes, but no evidence of oxidation, so holes are real. Again, no evidence of vapor phase deposition in tube.

The above understood  
and witnessed by \_\_\_\_\_

Date \_\_\_\_\_

and  
by \_\_\_\_\_

Date \_\_\_\_\_

IBM Technical Notebook

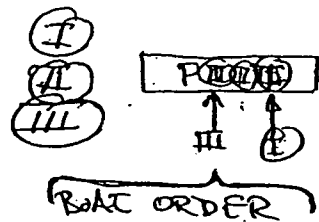
80 6/14/88

To do: 10, 20, 25 % in Ar/H<sub>2</sub>(s)

(VACATION)  
 MONDAY  
 RUN!

WENDS 6/22/88

5 gram batches: 0.25 (5) = 1.25 B. / 3.75 C  
 0.20 (5) = 1.00 B. / 4.00 C  
 0.10 (5) = .5 B. / 4.5 C



(I) 5 gram w/ new conical crucible  
 mix 9.03  
 tare 1.03  
 5.00  
 PRE

voids, but some areas seem OK.  
 less small voids, some good regions versus (II),  
 however larger voids & mystery. Need  
 repeating, maybe larger times.

(II)  
 9.00  
 tare 4.00  
 5.00

seems very good, no large voids, mic exam not  
 microscopic exam shows many small 'pockets'  
 or voids. Usually circular

(III) 6.31  
 tare 1.31  
 5.00 'nominal loss possible'

did not densify fully

## Scripps Milling Results

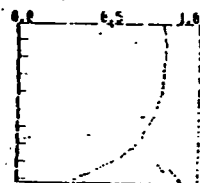
 MODEL CAPA-SEE  
 PARTICLE ANALYZER

 DATE 3/24/88  
 SAMPLE S-103-3  
 SOLVENT ISO  
 MT-MED
• CONDITIONS  
SIGHT IMPROVEMENT
 SOLV. VISC 2.10 (CP)  
 SOLV. DENS 0.7916 (CC)  
 SAMP. DENS 4.816 (CC)  
 D(CRACK) 16.8 (PP)  
 D(CHIP) 1.00 (PP)  
 D(CRIP) 1.00 (PP)  
 SPEED 500. (RPM)

• TIME 0 H 6 MIN 0 SEC

• DATE D=0.8

TIME ABSORBANCE

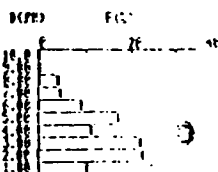


## • DISTRIBUTION TABLE (BY VOL.)

D(PH)	F(%)	R(%)
10.0 -	0.0	0.0
10.0 - 9.0	0.0	0.0
9.00-8.00	0.0	0.0
8.00-7.00	3.9	3.9
7.00-6.00	4.4	8.4
6.00-5.00	0.5	17.2
5.00-4.00	17.1	34.2
4.00-3.00	11.1	45.4
3.00-2.00	22.6	67.4
2.00-1.00	22.5	89.9
1.00-0.00	10.2	100.0

D(CRACK) 2.75 (PP)

## • DISTRIBUTION GRAPH (BY VOL.)


 MODEL CAPA-SEE  
 PARTICLE ANALYZER

 DATE 3/24/88  
 SAMPLE S-103-102  
 SOLVENT ISO  
 MT-S

## • CONDITIONS

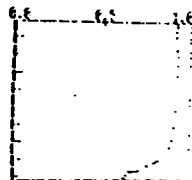
 SOLV. VISC 2.10 (CP)  
 SOLV. DENS 0.7916 (CC)  
 SAMP. DENS 4.816 (CC)  
 D(CRACK) 16.8 (PP)  
 D(CHIP) 1.00 (PP)  
 D(CRIP) 1.00 (PP)

SPEED 500. (RPM)

• TIME 0 H 6 MIN 0 SEC

• DATE

TIME ABSORBANCE

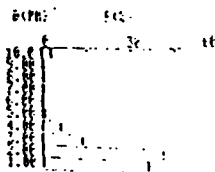


## • DISTRIBUTION TABLE (BY VOL.)

D(PH)	F(%)	R(%)
10.0 -	0.0	0.0
10.0 - 9.0	2.5	2.5
9.00-8.00	0.0	2.5
8.00-7.00	0.0	2.5
7.00-6.00	0.0	2.5
6.00-5.00	0.0	2.5
5.00-4.00	0.0	2.5
4.00-3.00	5.5	5.5
3.00-2.00	12.4	20.0
2.00-1.00	41.0	64.0
1.00-0.00	32.5	100.0

D(CRACK) 1.34 (PP)

## • DISTRIBUTION GRAPH (BY VOL.)


 MODEL CAPA-SEE  
 PARTICLE ANALYZER

 DATE 3/24/88  
 SAMPLE S-103-102  
 SOLVENT ISO  
 MT

## • CONDITIONS

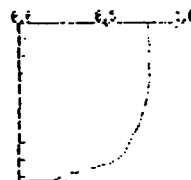
 SOLV. VISC 2.10 (CP)  
 SOLV. DENS 0.7916 (CC)  
 SAMP. DENS 4.816 (CC)  
 D(CRACK) 16.8 (PP)  
 D(CHIP) 1.00 (PP)  
 D(CRIP) 1.00 (PP)

SPEED 500. (RPM)

• TIME 0 H 6 MIN 0 SEC

• DATE

TIME ABSORBANCE

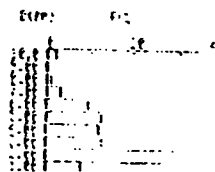


## • DISTRIBUTION TABLE (BY VOL.)

D(PH)	F(%)	R(%)
10.0 -	0.0	0.0
10.0 - 9.0	1.0	1.0
9.00-8.00	0.0	1.0
8.00-7.00	1.0	2.0
7.00-6.00	2.5	5.0
6.00-5.00	5.5	15.0
5.00-4.00	12.5	27.5
4.00-3.00	12.1	35.6
3.00-2.00	12.6	52.0
2.00-1.00	19.0	72.0
1.00-0.00	7.5	100.0

D(CRACK) 2.20 (PP)

## • DISTRIBUTION GRAPH (BY VOL.)



Administrative Notes

C3 Milling RESULTS - T1: TeFlon T2: Polyu T3: PolyN

T1

NOIRIS CAPP-SET  
PARTICLE ANALYZER

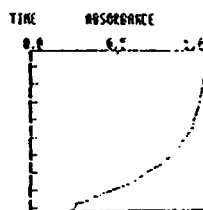
DATE 5/17  
SAMPLE C3-PV  
SOLVENT ISO

• CONDITIONS

T1 →  
SOLV. VISC 2.18 (CP)  
SOLV. DENS 0.7916 (CC)  
SAMP. DENS 0.3616 (CC)  
D(CMAX) 10.0 (PM)  
D(CMIN) 1.00 (PM)  
D(CDIV) 1.00 (PM)  
SPEED 500. (RPM)

• TIME 0 H 4 MIN 20 SEC

• DATA

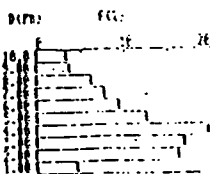


• DISTRIBUTION TABLE (BY VOL.)

D(PH)	F(2)	R(2)
10.0 <	0.0	0.0
10.0-9.0	3.3	3.2
9.00-8.00	3.6	6.9
8.00-7.00	6.1	13.0
7.00-6.00	7.7	20.7
6.00-5.00	9.5	30.2
5.00-4.00	12.6	42.8
4.00-3.00	15.6	58.4
3.00-2.00	16.8	75.2
2.00-1.00	16.2	91.4
1.00-0.00	4.6	100.0

D(AVE) 3.43 (PM)

• DISTRIBUTION GRAPH (BY VOL.)



NOIRIS CAPP-SET  
PARTICLE ANALYZER

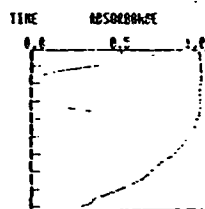
DATE 5/17  
SAMPLE C3-PV  
SOLVENT IS

• CONDITIONS 0.097

SOLV. VISC 2.18 (CP)  
SOLV. DENS 0.7916 (CC)  
SAMP. DENS 0.3616 (CC)  
D(CMAX) 10.0 (PM)  
D(CMIN) 1.00 (PM)  
D(CDIV) 1.00 (PM)  
SPEED 500. (RPM)

• TIME 0 H 4 MIN 20 SEC

• DATA

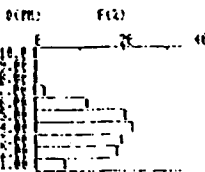


• DISTRIBUTION TABLE (BY VOL.)

D(PH)	F(2)	R(2)
10.0 <	0.0	0.0
10.0-9.0	0.0	0.0
9.00-8.00	0.0	0.0
8.00-7.00	0.0	0.0
7.00-6.00	2.1	2.1
6.00-5.00	11.5	13.6
5.00-4.00	26.2	33.8
4.00-3.00	21.5	55.7
3.00-2.00	15.4	71.1
2.00-1.00	10.3	81.4
1.00-0.00	6.6	100.0

D(AVE) 3.26 (PM)

• DISTRIBUTION GRAPH (BY VOL.)



NOIRIS CAPP-SET  
PARTICLE ANALYZER

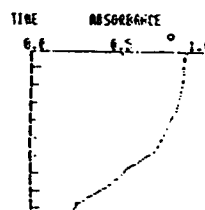
DATE 5/17  
SAMPLE C3-PV  
SOLVENT ISO

• CONDITIONS 0.09

SOLV. VISC 2.18 (CP)  
SOLV. DENS 0.7916 (CC)  
SAMP. DENS 0.3616 (CC)  
D(CMAX) 10.0 (PM)  
D(CMIN) 1.00 (PM)  
D(CDIV) 1.00 (PM)  
SPEED 500. (RPM)

• TIME 0 H 4 MIN 20 SEC

• DATA

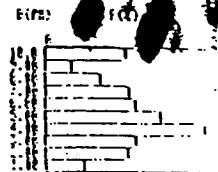


• DISTRIBUTION TABLE (BY VOL.)

D(PH)	F(2)	R(2)
10.0 <	0.0	0.0
10.0-9.0	0.0	0.0
9.00-8.00	2.0	21.0
8.00-7.00	6.0	27.0
7.00-6.00	9.2	36.0
6.00-5.00	9.0	45.0
5.00-4.00	12.6	57.6
4.00-3.00	17.6	75.2
3.00-2.00	9.0	84.2
2.00-1.00	9.0	93.0
1.00-0.00	4.2	100.0

D(AVE) 4.73 (PM)

• DISTRIBUTION GRAPH (BY VOL.)



T2 Part I

MOP104 CAPA-504  
PARTICLE ANALYZERDATE 5/19  
SAMPLE C3-PI-T2  
SOLVENT 150

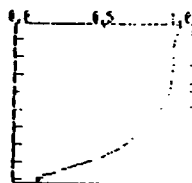
## • CONDITIONS

SOLV. VISC 2.10 cP  
SOLV. DENS 0.7916 g/cc  
SAMP. DENS 0.3616 g/cc  
D(CHX) 10.0 cP  
D(CHN) 1.00 cP  
D(CHV) 1.00 cP  
SPEED 500 cP

• TIME 0 H 4 MIN 26 SEC

• DATE ~0.9

TIME RESONANCE

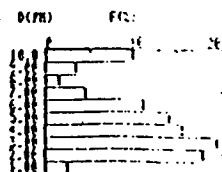


## • DISTRIBUTION TABLE (BY VOL.)

D(CPH)	F(C)	F(C)
10.0-9.0	0.0	0.0
9.0-8.0	0.0	0.0
8.0-7.0	1.5	14.6
7.0-6.0	4.5	15.2
6.0-5.0	11.2	36.4
5.0-4.0	14.1	44.7
4.0-3.0	15.6	48.1
3.0-2.0	15.4	79.5
2.0-1.0	10.0	57.5
1.0-0.0	2.5	100.0

D(CHE) 3.65 cP

## • DISTRIBUTION GRAPH (BY VOL.)

MOP104 CAPA-504  
PARTICLE ANALYZERDATE 5/19  
SAMPLE C3-PI-T2  
SOLVENT 150

## • CONDITIONS

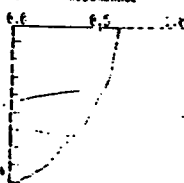
SOLV. VISC 2.10 cP  
SOLV. DENS 0.7916 g/cc  
SAMP. DENS 0.3616 g/cc  
D(CHX) 10.0 cP  
D(CHN) 1.00 cP  
D(CHV) 1.00 cP

• SPEED 500 cP

• TIME 0 H 4 MIN 26 SEC

• DATE ~0.57

TIME RESONANCE

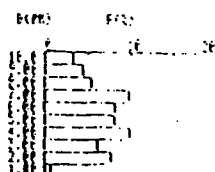


## • DISTRIBUTION TABLE (BY VOL.)

D(CPH)	F(C)	F(C)
10.0-9.0	0.0	0.0
9.0-8.0	0.0	0.0
8.0-7.0	1.5	14.6
7.0-6.0	4.5	15.2
6.0-5.0	11.2	36.4
5.0-4.0	14.1	44.7
4.0-3.0	15.6	48.1
3.0-2.0	15.4	79.5
2.0-1.0	10.0	57.5
1.0-0.0	2.5	100.0

D(CHE) 6.94 cP

## • DISTRIBUTION GRAPH (BY VOL.)

MOP104 CAPA-504  
PARTICLE ANALYZERDATE 5/19  
SAMPLE C3-PI-T2  
SOLVENT 150

## • CONDITIONS

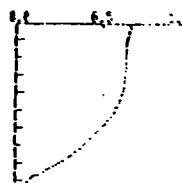
SOLV. VISC 2.10 cP  
SOLV. DENS 0.7916 g/cc  
SAMP. DENS 0.3616 g/cc  
D(CHX) 10.0 cP  
D(CHN) 1.00 cP  
D(CHV) 1.00 cP

• SPEED 500 cP

• TIME 0 H 4 MIN 26 SEC

• DATE ~0.67

TIME RESONANCE

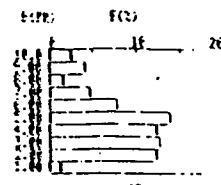


## • DISTRIBUTION TABLE (BY VOL.)

D(CPH)	F(C)	F(C)
10.0-9.0	0.0	0.0
9.0-8.0	0.0	0.0
8.0-7.0	1.5	14.6
7.0-6.0	4.5	15.2
6.0-5.0	11.2	36.4
5.0-4.0	14.1	44.7
4.0-3.0	15.6	48.1
3.0-2.0	15.4	79.5
2.0-1.0	10.0	57.5
1.0-0.0	2.5	100.0

D(CHE) 4.04 cP

## • DISTRIBUTION GRAPH (BY VOL.)



# Administrative Notes

TR PART 2

MODEL CAPA-504  
PARTICLE ANALYZER

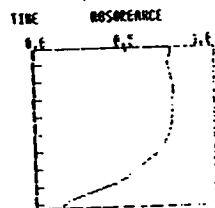
DATE 5/9  
SAMPLE CS-73-12  
SOLVENT 150

## • CONDITIONS

SOLV. VISC 2.10 (CP)  
SOLV. DENS 0.79 (G/CC)  
SAMP. DENS 6.36 (G/CC)  
D(CRX) 10.0 (PM)  
D(CIN) 1.00 (PM)  
D(DIV) 1.00 (PM)  
SPEED 500. (RPM)

• TIME 0 R 4 MIN 20 SEC

• DATE ~0.7

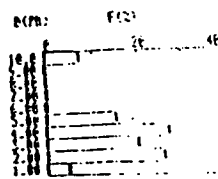


## • DISTRIBUTION TABLE (BY VOL.)

D(PM)	F(%)	R(%)
10.0 - 9.0	0.0	0.0
9.0 - 8.00	7.2	7.2
8.00 - 7.00	0.0	7.2
7.00 - 6.00	0.0	7.2
6.00 - 5.00	0.3	7.6
5.00 - 4.00	15.1	22.7
4.00 - 3.00	27.0	49.7
3.00 - 2.00	20.0	69.7
2.00 - 1.00	25.6	95.3
1.00 - 0.00	4.7	100.0

D(CRVE) 2.50 (PM)

## • DISTRIBUTION GRAPH (BY VOL.)



MODEL CAPA-504  
PARTICLE ANALYZER

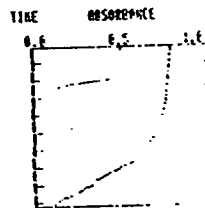
DATE 5/9  
SAMPLE CS-73-12  
SOLVENT 150

## • CONDITIONS

SOLV. VISC 2.10 (CP)  
SOLV. DENS 0.79 (G/CC)  
SAMP. DENS 6.36 (G/CC)  
D(CRX) 10.0 (PM)  
D(CIN) 1.00 (PM)  
D(DIV) 1.00 (PM)  
SPEED 500. (RPM)

• TIME 0 R 4 MIN 20 SEC

• DATE ~0.7



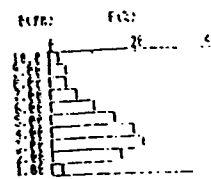
## • DISTRIBUTION TABLE (BY VOL.)

D(PM)	F(%)	R(%)
10.0 - 9.0	0.0	0.0
9.0 - 8.00	2.2	2.2
8.00 - 7.00	3.5	5.7
7.00 - 6.00	3.7	9.4
6.00 - 5.00	6.2	16.6
5.00 - 4.00	10.1	26.6
4.00 - 3.00	15.0	41.6
3.00 - 2.00	19.0	60.6
2.00 - 1.00	21.4	81.5
1.00 - 0.00	16.0	97.5
0.00 - 0.00	2.5	100.0

D(CRVE) 2.50 (PM)

NO MEANING / BIG CHANGE

## • DISTRIBUTION GRAPH (BY VOL.)



MODEL CAPA-504  
PARTICLE ANALYZER

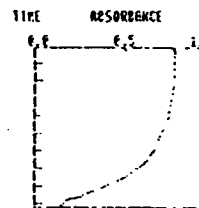
DATE 5/9/83  
SAMPLE CS-73-12  
SOLVENT 150

## • CONDITIONS

SOLV. VISC 2.10 (CP)  
SOLV. DENS 0.79 (G/CC)  
SAMP. DENS 6.36 (G/CC)  
D(CRX) 10.0 (PM)  
D(CIN) 1.00 (PM)  
D(DIV) 1.00 (PM)  
SPEED 500. (RPM)

• TIME 0 R 4 MIN 20 SEC

• DATE

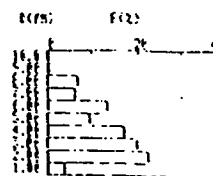


## • DISTRIBUTION TABLE (BY VOL.)

D(PM)	F(%)	R(%)
10.0 - 9.0	0.0	0.0
9.0 - 8.00	0.0	0.0
8.00 - 7.00	0.0	0.0
7.00 - 6.00	0.0	0.0
6.00 - 5.00	12.4	12.4
5.00 - 4.00	5.6	18.0
4.00 - 3.00	17.1	35.1
3.00 - 2.00	26.0	61.1
2.00 - 1.00	22.4	83.5
1.00 - 0.00	4.6	100.0

D(CRVE) 3.21 (PM)

## • DISTRIBUTION GRAPH (BY VOL.)





T2 (cont.)

HORIBA EMP-500  
PARTICLE ANALYZERDATE  
SAMPLE CS-P5-T2  
SOLVENT

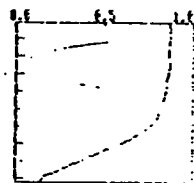
## • CONDITIONS

SOLV. VISC 2.10 (CP)  
 SOLV. DENS 0.79 (G/CC)  
 SAMP. DENS 6.36 (G/CC)  
 D(CRX) 10.0 (PH)  
 D(CIN) 1.00 (PH)  
 D(CIV) 1.00 (PH)  
 SPEED 500 (RPM)

• TIME 6 H 4 MIN 26 SEC

• DATE 0.87

TIME ABSORBANCE

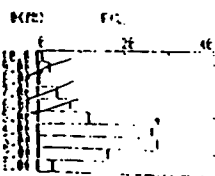


## • DISTRIBUTION TABLE (BY VOL.)

D(PH)	F(%)	G(%)
10.0-9.0	0.0	0.0
9.0-8.0	1.2	1.2
8.0-7.0	2.6	3.8
7.0-6.0	8.1	11.9
6.0-5.0	14.4	26.3
5.0-4.0	21.8	48.1
4.0-3.0	26.2	74.3
3.0-2.0	27.3	101.6
2.0-1.0	15.1	116.7
1.0-0.0	3.4	120.1

D(CRV) 3.14 (PH)

## • DISTRIBUTION GRAPH (BY VOL.)

HORIBA EMP-500  
PARTICLE ANALYZERDATE 5/19  
SAMPLE CS-P5-T2  
SOLVENT

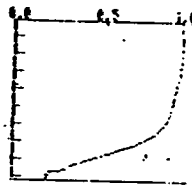
## • CONDITIONS

SOLV. VISC 2.10 (CP)  
 SOLV. DENS 0.79 (G/CC)  
 SAMP. DENS 6.36 (G/CC)  
 D(CRX) 10.0 (PH)  
 D(CIN) 1.00 (PH)  
 D(CIV) 1.00 (PH)  
 SPEED 500 (RPM)

• TIME 0 H 4 MIN 26 SEC

• DATE 0.9

TIME ABSORBANCE

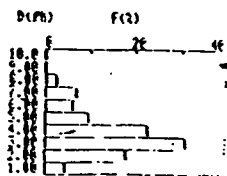


## • DISTRIBUTION TABLE (BY VOL.)

D(PH)	F(%)	G(%)
10.0-9.0	0.0	0.0
9.0-8.0	0.0	0.0
8.0-7.0	0.0	0.0
7.0-6.0	2.2	2.2
6.0-5.0	6.0	8.2
5.0-4.0	9.6	17.8
4.0-3.0	22.5	40.3
3.0-2.0	36.1	76.4
2.0-1.0	40.6	117.0
1.0-0.0	4.3	121.3

D(CRV) 2.91 (PH)

## • DISTRIBUTION GRAPH (BY VOL.)



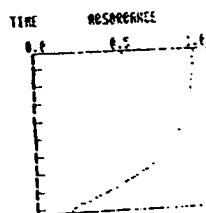
## Administrative Notes

T1 versus T2 versus T3 for various passes

NOR100 CAPP-SEC  
PARTICLE ANALYZERDATE APR  
SAMPLE C3-PI-B  
SOLVENT ISO• CONDITION (T3)  
SOLV. VISC 2.10(CP)  
SOLV. DENS 0.7916(CC)  
SAMP. DENS 6.3616(CC)  
D(ARX) 10.0 (PP)  
D(ARF) 1.00(CP)  
D(ARV) 1.00(CP)  
SPEED 500. (CPH)

• TIME 0 H 4 MIN 20 SEC

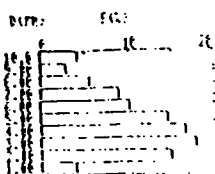
• DATA 0.9



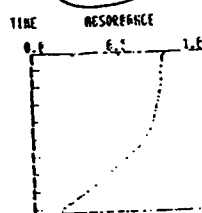
• DISTRIBUTION TABLE (BY VOL.)

D(PH)	F(2)	F(3)
10.0 - 9.0	0.0	0.0
9.0 - 8.0	4.2	4.2
8.0 - 7.0	2.5	7.0
7.0 - 6.0	5.0	12.0
6.0 - 5.0	10.0	22.0
5.0 - 4.0	14.0	36.0
4.0 - 3.0	16.0	52.0
3.0 - 2.0	17.5	69.5
2.0 - 1.0	15.0	84.5
1.0 - 0.0	4.0	100.0
D(AVE)	3.79 (PP)	

• DISTRIBUTION GRAPH (BY VOL.)

NOR100 CAPP-SEC  
PARTICLE ANALYZERDATE 5/12  
SAMPLE C3-PIV  
SOLVENT• CONDITION 0.85  
SOLV. VISC 2.10(CP)  
SOLV. DENS 0.7916(CC)  
SAMP. DENS 6.3616(CC)  
D(ARX) 10.0 (PP)  
D(ARF) 1.00(CP)  
D(ARV) 1.00(CP)  
SPEED 500. (CPH)

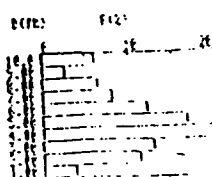
• TIME 0 H 4 MIN 20 SEC

• DATA (T1)

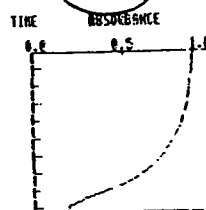
• DISTRIBUTION TABLE (BY VOL.)

D(PH)	F(2)	F(3)
10.0 - 9.0	0.0	0.0
9.0 - 8.0	0.0	0.0
8.0 - 7.0	2.0	2.0
7.0 - 6.0	6.0	8.0
6.0 - 5.0	6.0	14.0
5.0 - 4.0	12.0	26.0
4.0 - 3.0	16.0	42.0
3.0 - 2.0	12.0	58.0
2.0 - 1.0	11.0	69.0
1.0 - 0.0	3.0	100.0
D(AVE)	4.14 (PP)	

• DISTRIBUTION GRAPH (BY VOL.)

NOR100 CAPP-SEC  
PARTICLE ANALYZERDATE 13-PIV  
SAMPLE  
SOLVENT• CONDITION NO CHANGE  
NO CHANGE REQUIRED  
SOLV. VISC 2.10(CP)  
SOLV. DENS 0.7916(CC)  
SAMP. DENS 6.3616(CC)  
D(ARX) 10.0 (PP)  
D(ARF) 1.00(CP)  
D(ARV) 1.00(CP)  
SPEED 500. (CPH)

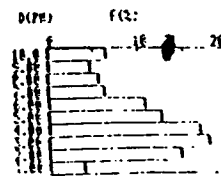
• TIME 0 H 4 MIN 20 SEC

• DATA (T2)

• DISTRIBUTION TABLE (BY VOL.)

D(PH)	F(2)	F(3)
10.0 - 9.0	0.0	0.0
9.0 - 8.0	0.0	0.0
8.0 - 7.0	4.7	4.7
7.0 - 6.0	5.0	9.7
6.0 - 5.0	6.3	15.7
5.0 - 4.0	12.7	28.4
4.0 - 3.0	16.5	44.9
3.0 - 2.0	16.0	60.9
2.0 - 1.0	14.7	75.6
1.0 - 0.0	3.0	100.0
D(AVE)	3.79 (PP)	

• DISTRIBUTION GRAPH (BY VOL.)



FINAL **C3-T3** - RESULTS: NECIC, MIX { premix medium

NO. 100  
PARTICLE

SAMPLE  
SOLVENT

## • CONDITIONS

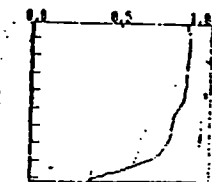
SOLV. VISC 2.10 (CP)  
SOLV. DENS 0.79 (G/CC)  
SAMP. DENS 6.36 (G/CC)  
D(CMAX) 10.0 (PP)  
D(CMIN) 1.00 (PP)  
D(CDIV) 1.00 (PP)  
SPEED 500. (RPM)

NECK

• TIME 0 H 4 MIN 20 SEC

## • DATA

TIME ABSORBANCE



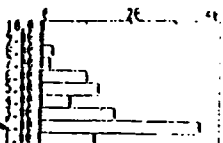
## • DISTRIBUTION TABLE (BY VOL.)

D (PP)	F (2)	R (2)
10.0-9.0	0.0	0.0
9.00-8.00	0.0	0.0
8.00-7.00	2.4	2.4
7.00-6.00	13.6	4.4
6.00-5.00	10.5	14.5
5.00-4.00	13.1	20.6
4.00-3.00	6.5	34.5
3.00-2.00	17.6	51.5
2.00-1.00	9	67.4
1.00-0.00	106.0	106.0

D(AVE) 2.09 (PP)

## • DISTRIBUTION GRAPH (BY VOL.)

D (PP) F (2)



NO. 100  
PARTICLE ANALYZER

DATE 5/22  
SAMPLE C3-T3-MIX  
SOLVENT P32

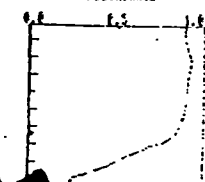
## • CONDITIONS

SOLV. VISC 2.10 (CP)  
SOLV. DENS 0.79 (G/CC)  
SAMP. DENS 6.36 (G/CC)  
D(CMAX) 10.0 (PP)  
D(CMIN) 1.00 (PP)  
D(CDIV) 1.00 (PP)  
SPEED 500. (RPM)

• TIME 0 H 4 MIN 20 SEC

• DATA *DN 0.9*

TIME ABSORBANCE



## • DISTRIBUTION TABLE (BY VOL.)

D (PP)	F (2)	R (2)
10.0-9.0	0.0	0.0
9.00-8.00	1.2	1.2
8.00-7.00	0.6	1.2
7.00-6.00	0.6	1.2
6.00-5.00	0.6	1.2
5.00-4.00	5.7	16.5
4.00-3.00	27.7	30.6
3.00-2.00	65.6	65.6
2.00-1.00	52.7	52.7
1.00-0.00	106.0	106.0

D(AVE) 2.62 (PP)

## • DISTRIBUTION GRAPH (BY VOL.)

D (PP) F (2)



NO. 100  
PARTICLE ANALYZER

DATE 5/22  
SAMPLE C3-T3-T3  
SOLVENT ISO

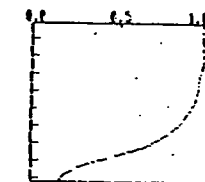
## • CONDITIONS

SOLV. VISC 2.10 (CP)  
SOLV. DENS 0.79 (G/CC)  
SAMP. DENS 6.36 (G/CC)  
D(CMAX) 10.0 (PP)  
D(CMIN) 1.00 (PP)  
D(CDIV) 1.00 (PP)  
SPEED 500. (RPM)

• TIME 0 H 4 MIN 20 SEC

## • DATA

TIME ABSORBANCE



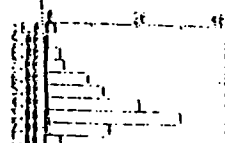
## • DISTRIBUTION TABLE (BY VOL.)

D (PP)	F (2)	R (2)
10.0-9.0	0.0	0.0
9.00-8.00	1.6	1.6
8.00-7.00	2.1	4.9
7.00-6.00	4.3	5.2
6.00-5.00	9.4	10.6
5.00-4.00	12.6	31.5
4.00-3.00	20.7	52.2
3.00-2.00	36.6	62.2
2.00-1.00	14.3	96.5
1.00-0.00	3.5	100.0

D(AVE) 3.11 (PP)

## • DISTRIBUTION GRAPH (BY VOL.)

D (PP) F (2)



100179

Technical Notebook

Book V

Initials and Last Name:

NCOMBE, P.

Serial:

139

Date of First Entry:

6/7/88

Date of Last Entry:

5/89

Security Classification:

42 11-17-88

IBM Technical Notebook

Survey 2212 sintering time versus rel density

<u>h</u>	<u>rel D(%)</u>	<u>wt</u>
0	68.4	
✓ (0.08)	65.9	6.97
✓ 0.25	61.1	
✓ 0.5	59.7	
(16) (70)	54	
✓ 120	51	

small pellet, density determination probably not as accurate

16h (not listed in book)

POST

0.88 1.15 0.216 0.22 4.0 / 6.45 62

REDO

11-2-88 0011 Analytical IBM Technical Notebook

El.	wt %	theo. M%	ANA M%
Ca	22.4	0.86	0.875
Sr	8.24	0.14	0.147
C	40.6	1	1

Example calc. ✓  
 $\frac{Ca\ wt\ \%}{C_{total}} = \frac{0.639}{0.639} = 1$   
 $\frac{Sr\ wt\ \%}{C_{total}} = \frac{0.094}{0.639} = 0.147$   
 $\frac{C\ wt\ \%}{C_{total}} = \frac{0.539}{0.539} = 0.875$

11/3 0011 pellet 2 for 16h diffusion sinter  
 Pre 4000/30,000 slightly irregular

2.85	1.531	0.496	0.913	~3.12	/4.95 = 63 — perfect
2.81	~1.36	0.44	0.639	4.4	↓ = <u>89</u>
			0.64		

0201 4,000/30,000 PRE

3.78	1.365	0.494	0.723	5.23	= 72.4% (too high?)
------	-------	-------	-------	------	---------------------

11/4 0011-2 cut into 2 slices. Didn't add block thickness so irregular.  
 1 ~ 2.30 cm thick 1 ~ 0.179 cm

↓ Post will use for first press  
 875C for 30 hrs → pellet has warped, grown large voids like xstals and sagged. Obviously metastable.

previous 3h sinter showed no evidence of instability.

~~11-2-88~~


IBM Technical Notebook

44 11-9 2201 pellets  
 3200/28  
 2013 2.99 1.351 0.415 0.595 5.02 69.7  
 2.96 ~1.306 0.372 0.498 ~5.98 ~83.3+  
 2013 MIN 872C SINTER (SLD ATTAINMENT 12 MIN TERSUS 1. T<sub>int</sub> = T<sub>AT</sub> + 3 min)  
 open possibly  
 pycnometer  
 86  
 air = 85

3300/30  
 2014 1.16 1.082 0.245 0.225 5.16 71.7  
 1.15 1.050\* 0.210\* 0.182 6.32  
 87.5  
 5 min.  
 double

2015 1.17 1.086 0.248 0.230 5.09 70.7  
 { broken before  
 sintering  
 reground  
 repressed } pellet 201-112

2016 0.99 1.094 0.205 0.193 5.13 71.25  
 \*† 0.98 1.06 0.185<sup>1p</sup> 0.163 6.01  
 \* (0.178) 0.158 6.2  
 83.5  
 86  
 to temp 1845  
 out 2.15  
 36 min

\*(†): 201-4/5 some evidence of drooping  

 edge droop  
 in pellet. reduce temp 5C

2700/29  
 2017 1.2 1.087 0.258 0.238(5) 5.03 69.9  
 1.01 ~1.05 0.185 0.165  
 1.06 1.19 1.05 ~0.225 0.195 6.1 84.7  
 to temp 2727-8  
 15  
 2.145  
 15

# 11-10 Sintering Summary <2201 data>

45

	temp	SINTER	green	POST.	201-2
201-8	872C	2min	71.25	85.6	C11-2201 P3 pressed pellet (large die) 86.1ave
201-3	872	12-3	69.7	86	
201-4	875C	5	71.7	87.5	
201-9	872C	5	71-	84.7	
201-7	872C	15	69.9	84.7	
201-6	875C	30	71.25	83.5	
201-10	872C	1h	70.4	86.7 → 85	
201-1	875C	2h		84-	
201-2	875	30h		(76.1) → 79	

not sintered  
2h  
3h

Record keeping: 201-2 30h 875C ~ 75% (pyc): irregular pellet growth  
resulting in varying local densities  
201-3 0.608 dia. pellet for pressure diffusion sinter  
201-5 regd → 201-11

11-11 GAS pycnometry gives an averaged rel density for pellets 1, 7, 8, 9  
(wght 4.6g) of 86.75g vs 84.75 (reasonable agreement), mostly  
closed porosity.

The above understood  
and witnessed by

Date

and  
by

Date



46  
11-14 SINTER 870-875°C IBM Technical Notebook

NOTE: ALL SINTER TIMES ARE 1 MW attainment +  
1 MW EQ SOAK +  $\Delta$  SINTER time

201-8 perfect pellet ~3000/29000

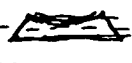
POST	1.19	1.081	0.253	0.232	5.13	71.25	green
2 MIN	1.17	1.038	0.225	0.190	6.16	85.6	

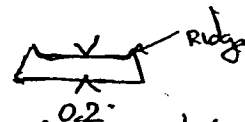
POST	201-9 12	1.075	0.259	0.235	5.11	71.00	green
5 MIN	1.09	1.036	0.231	0.195	6.10	84.7	

POST	201-10 1.10	1.083	0.236	0.217	5.07	70.4	
1h	1.09	1.057*	0.2+	0.175(5)	6.21	86.25 (accurate?)	see below

201-11 Pellet was reg'd & repressed from broken pellet. Also, die ran from result, i.e. in much higher uniaxial pressure (if true edge) 12,000

1.169	0.252	0.24	5.04	70.00
-------	-------	------	------	-------

\* linear average dia due to slumping. (-   
† w pellet interior after edge ridge worn away



? probably slightly less due to exclusion of ridge volume and linear average approx. after flattening; 15  $\mu$ m

201-10	0.90+	1.057	0.168	0.147	6.12	85	better (more accurate)
--------	-------	-------	-------	-------	------	----	------------------------

201-11	1.357	0.412	0.596	4.	49.6	5.0	(69.4)
--------	-------	-------	-------	----	------	-----	--------

2.935	1.315	0.365	0.496	5.94	82.5
2.945					

11-12

201-11 cut "whisk" longer flattened and polished.

0011-2201 sandwich ~0.353-0.363 thick.

> From furnace top to bottom of "weight plate"  $1\frac{7}{32}$ " @ 462C  
assuming ~6 lbs. force RAM & plate & x-sectional pellet area  
of  $0.212 \text{ in}^2$  load  $\Rightarrow$  28 psi

Diffusion sintering set @ 860C for ~12 hrs.

Rel density from measurement of 201-11 ~83%. On inspection  
of internal polished surface numerous burnout-like occlusions present.  
Some degree of open porosity, also.

Pyc. rel. den = 88. % this  $\Delta$  attributable to open porosity.

0011 rel density from measure ~89%. No pyc reading done  
16h sinter @ 975C.

4:30 pm T @ 859C assume start of diffusion sintering

Plate height  $1\frac{3}{8}$ " ( $\frac{3}{32}$ " expansion due to TCE from 462C)  
(No RT measure made, but not significant)

48

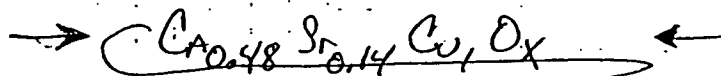
IBM Technical Notebook

11-28-88 <INSERT>

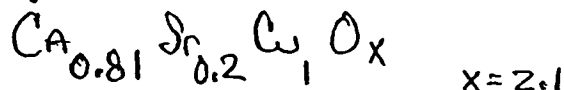
Results (by microprobe) of  $\text{CaSrCuO}_x$  melt xstals

Melt composition was from pgs. 27-29

Composition was not  $\text{Ca}_{0.86}\text{Sr}_{0.14}\text{Cu}_1\text{O}_x$  in melt, but rather



from which xstals grew of  $\text{CaSrCuO}_x$  with stoic.



Atomic weight fractions were:

Ca	0.195
Sr	0.05
Cu	0.242
O	0.513 (by difference)

Melt temp. was 1000C for 16h with cooling virtually, but  
 NOT TOTALLY A QUENCH. UNCONTROLLED RATE REGULATED BY PLENOR  
 thermal mass

11-22

Balance Bi Powders for Run

2212 - <sup>~g</sup>30.5

2201 - 12.5

0011 - 33.5

2<sup>nd</sup> Diffusion Run 2hr ramp to 866C @ 100C plate space = 1 7/32

0011 slice studied @ 0.18 cm (not measured when finished, either was 2201 or sandwich, will try to approx)

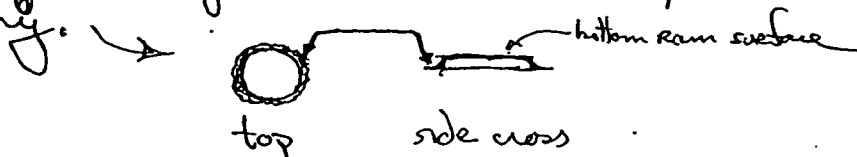
2201 ~ same 0.18

loose ~ 0.23 - 0.2 x 0.03/slice ∴ 0.18 → 0.15 0.17 → 0.14  
 so sandwich might be ~ 0.29 cm (80% of run #1)

Approx thickness by height of plate differences @ 866C 1 12/32 - 1 9/32

12/32 - 9/32 = 0.23 cm ∴ 0.29 - 0.23 = 0.06 too small → 871C peak

RESULTS: "Bi" pellet has spread, apparently melting. Total thickness 0.18 cm.  
 has generated crystalline (?) skirt around pellet periphery.



0.18 cm = 0.07" slice ~ square 0.07 + 0.015 = 0.085

50

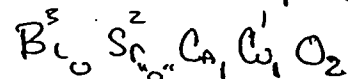
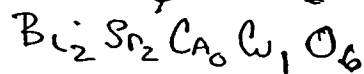
IBM Technical Notebook

0011-2201 Mix Calculations

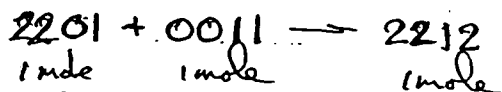
wt%      wt%  
 0011      2201

\*✓ +2

\*✓ +5



From "ideal" state.



	A.W.	0011	2201	2212
B <sub>1.2</sub>	208.98	-	417.96	417.96
Sr	87.62	-	175.24	175.24
Ca	40.08	40.08	-	40.08
C	63.54	63.54	63.54	127.08
O	15.9994		95.9964	127.9952

$$135.6188 + 752.7341 = 888.3552$$

B <sub>1.2</sub>	0(0.14)(0.86)1	(2.15)(1.6)(0)(1)	(2.15)(1.6)(1.17)(2)
	449.307	449.307	449.307
Sr	12.2168	140.192	147.2016
Ca	34.488	-	40.32816
C	63.54	63.54	127.08
O	31.9988	~95.9964*	*127.9952

142.2744      749.0354      891.912296 / (891.3098)

% dev      + 8.6%      99.6% (2.15 etc)

The above understood and witnessed by

Date

and

Date

IBM Technical Notebook

51

CONTINUATION...

1 mole "0011" + 1 mole 2201  $\rightarrow$  011 + 529 wt% 2201

142.2744g

752.7364g

$$142.2744g + (0.02)(142.2744) = 145.12g$$

2.84549

2 wt%

Batch  
15

9.49

9.485

0.19

9.675

batch size

$$142.2744g + (0.05)(142.2744) = 149.38812g$$

7.11372

5 wt%

9.485

~0.475

9.96

batch size

\*

0.48

For Stoic (molar) mix =  $1.423g + 7.53g = 8.95g$  batch size

Total Usage

0011

2201

8

20.393

8.192

8

%

61

66

	cc	cc	vol%	wt%
roll	2.37	0.0264	1.0%	2
table	2.37	0.0736	3	5
	0.356	1.045	25%	storic

STOIC: ~~2201~~ 2.15 1.6 0 1

"0011" 0 0.14 0.86 1

2.15 1.74 0.86 2 versus poly. 2.15 1.68 1.17 2

The above understood and witnessed by

Date

and hv

Date

## 52 Stoic Mixing

IBM Technical Notebook

0011 2201

~1.43 g ~7.53

MIX STARTING @ 3:00 P.M., 50mls isopropyl  
5cc  $ZrO_2$  balls  
2/3 full

NOTE: From bottom pg 51 can be seen this Additive approach will  
yield a theoretical molar comp { 0.1 M larger in Sr  
0.31 M less in Ca

i.e. Strontia rich, Calcium poor

8.96 g added initially, 8.85 g recovered: 1.2% loss (98.8 yield)

Stoic 1 Pre 2700/27,500

3.11 1.36 0.486 0.706 4.41 ~68.9

$0.25(4) + 0.75(7.2) = 6.4$  vol % basis, ~ density calc

Rxn. (SINTER) temp to be 850°C

Pellet melted indicating lower mp,  $1/2 \phi$  exists in system, later  
x-rayed. Predominantly 1 lath-like  $\phi$  w/ exaggerated growth  
as in 2201 120h sample.

12-5

4:20 P.M. // 4:25 @ temp.

0011-3 placed in preheated rapid temp set @ 951C ( $T_{\text{imp}} = 975C$ )  
for overnite sintering.  
No per data on density due to irregular shape caused by pellet crumbling during isopressing.  
unipress  $\rightarrow 6000, 150 - 29,000$  PSI wght  $\sim 3.1g$  <sup>3.0-2.9</sup>

12/6

9:30 Slow cooling begun  $\therefore \Delta T_{\text{inter}} = 17h @ 875C$

Post 2.86g  $\sim 0.460$  mm thick radius might have been  $\sim 1.58$

estimated density  $0.666cc @ 3.1g \sim 4.68/4.00 \approx 93$  (may be high)  
 $3.0 \quad 4.5 \downarrow \quad 90$  better

0011-3

0.181" thick

Slice 1  $\rightarrow 0.09$ " after cleaning // post polish  $\rightarrow$  N/R

Slice 2  $\rightarrow 0.074$   
 $0.179$  ✓

2201-8

1.038 dia  $\therefore$  area =  $\pi D^2/4 = 0.85 \text{ in}^2$   
 $0.409 \quad = 0.525 \text{ in}^2 \quad 5.75 \text{ lbs} / .525 \text{ in}^2 \sim 11 \text{ psi}$

2201-8 (top)



Pellet configuration @ start  $\sim 3:55$  p.m. thickness - 0.34 mm

0011-3

Ramp  $\rightarrow 434$  Set point - 800C Dwell - 12h  $1\frac{1}{2} @ 380C$

12/7 Result: no melting, pellets bonded by little deformation.

12/8

After 24h 825C Anneal no evidence of lica., but bond breaks after handling at pellet interface with some "rxn etching" of 0011 pellet surface having thin, <sup>upper</sup> layer of 2201 (or rxn prod) behind.



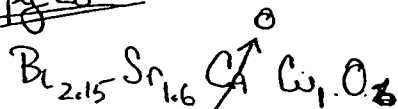
54  
12-6

IBM Technical Notebook

~~4/18/80~~

SECOND 2201 Synthesis

Ref pg 25



$\text{Bi} \approx \text{Bi}_2\text{O}_3 : 30.0543 \times 2 = 60.1086 \quad 60.11$

$\text{Sr} @ \text{SrCO}_3 : 14.1724 \quad 28.3448 \quad 28.35$

$\text{Cu} @ \text{CuO} : \frac{4.7724}{48.9991 \text{ g}} \quad \frac{9.5448}{97.9982 \text{ g}} \quad 9.54$

$\sim 0.7019 \text{ conversion factor for } \text{CO}_2 \rightarrow 0 \quad 28.3448 (0.702) = 19.898$

Estimate  $\sim 89 \text{ g}$  "batch recovery"  $\frac{97.9982}{89.55} \text{ CO}_2 \text{ loss}$

12-7

$\text{Bi}_2\text{O}_3$   $\frac{202.54}{262.68}$   
 $60.13 - 60.11 = +0.02 \checkmark$

$\text{SrCO}_3$   $\frac{291.03}{262.68}$   $\sim 27.38.35$  wgt  $28.36$  twofold  $28.36$   
 $28.35 \quad \Delta \checkmark$

$\text{CuO}$   $\frac{300.57}{291.03}$   $(300.57/9.54)$  wgt  $9.55$   
 $9.54 \quad \Delta \checkmark$

12-8  $97.92 / \text{recovery after drying overnite}$   
 $98.02 \text{ theoretical} = 99.9\% \text{ yield} \quad 0.1\% \text{ mixing loss}$

to pg 56

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and witnessed by

Date

and

Date

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55

12-7-88

011  
9.49  
9.48  
0.02  
9.46

011

2201  
0.48  
0.50  
0.01  
0.49

theor.

wtd

Reed

actual = 9.95

std. 1.5h 5min ZnO<sub>2</sub>/Iso  
grind mix, screening & drying.

12-8-88

Recovery : 9.84 g / 9.86 g theoretical = 99.8% > 0.2% loss

60.87  
cont tare 51.04/5  
9.83 transferred

0011-2201-5W(3V)-1

Post 8500/29,000

2.31 1.17 0.704 0.690 3.35 ~67%

Pellet bigger than usual, 1.75g max in future might be considered.

1.183 0.715 CRACKED, measurements ~~1.183~~

12-9

5W-2 900C 8500/39000

1.27 1.174 0.382 0.414 3.07 61.4!

3:55 in preheated furnace → 4:00 to temp @ 900C  
Post 5 min

1.24 1.11 0.36 0.349 3.55 71—

15 min NO SIGNIFICANT CHANGE

12-12 to temp ~ 10:20 A.M. (check: 10:45 → no slumping) → SWIR till 12:30

12:15 A.M. do-cool initiated

11:45

~2h

1.24 1.055 0.33 0.29 4.28 ~86%

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Date

and

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12-8-88 2201 SYNII cont. (from 1454)

crucible temp  $\begin{array}{r} 186.68 \\ - 88.79 \\ \hline 97.89 \end{array}$   $\xrightarrow{\text{spill}}$  186.68  $\rightarrow$  192.29 w/ tip

10:00 A.M.  $\rightarrow$  575C hold 1h  
 11:00  $\rightarrow$  800C  
 12-9 11:00 AM cool, required to < 100 mesh

$\begin{array}{r} 182.23 \\ - 88.95 \\ \hline 93.28 \end{array}$  (weight after sintered powder removed)

$\begin{array}{r} 93.44 \\ - 88.79 \\ \hline 4.65 \end{array}$  if 88.79 used  
 184.02 after grinding  
 $\begin{array}{r} 88.95 \\ - 93.28 \\ \hline -4.33 \end{array}$  to temp. (866C) @ 1:00 p.m.  
 $\Delta 1.21$  w/ grinding 1.3%  
 $97.88 - 93.28 = 4.6$   
 $97.89 - 89.55 = 8.34$  } 55% REACTED

1:00 - 5:00 pm 866C, shut down for weekend (very resistant saw eye)

12-12-88

to temp 866C @ 10:00 A.M.  
 off @ 7:00 A.M. 12/13/88

PARTIAL MELTING, "CLASSIC" EUTECTIC lamellar and large 2201 lathes.

Date and sign every entry. Have  
entry witnessed. Submit an Inver  
anything possibly not and cont.

y possibly important  
Disclosure of

☐ Unclassified  
☐ IBM Internal Use  
☐ Confidential

☐ IBM Confidential-Restricted  
☐ Registered IBM Confidential  
Register with local Recorder

~~12-14-88 2201 Sys III~~

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~~memory for bus: 202.75~~

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Date \_\_\_\_\_

and  
by \_\_\_\_\_

Date \_\_\_\_\_

58 12-14-88 **SYNTH 2201** IBM Technical Notebook

mixing jar tare 202.75

Bi as  $Bi_2O_3$  30.0543

Sr as  $SrCO_3$  14.1724

C. as  $CoO$  4.7724

x 2 = 60.11

28.35

9.55

98.01

- 8.5  $CO_2$  loss

89.51

$Sr/Bi = 0.744$

$Sr 0.8 Sr = 1.72$

$Bi_2O_3$  262.86

tare 202.75

60.11

291.20(19)

262.86

28.34(5)

300.75

291.20

9.55

PRE CAL I

crucible + 185.84

tare 87.99

97.85

$97.85/98.01 = 0.2\%$  max loss

12-20 Post 750C 16h calcination

crucible + 181.15

↓

87.98

93.17

post gen 92.70

NO RXN w/ Pt. ; lime green color/bottom, uniform throat

except for top 1/2 edges (grey)  
 $93.17 - 97.85 = -4.68 / 8.5 = 55\%$   $CO_2$  lost

post gr

crucible + 180.70

↓

87.98

(92.72)

12-21-88 Post 790C 20h calcination

178.10

87.98

90.12

Material looks very good, smooth indicating lamellar structure  
 Uniformly black, sparkling, smooth body. An outer shell  
 89% RXN close to completion # 98%  
 and inner core structure. (see below)



inner sub-core  
 outer shell  
 air space

The above understood  
 and witnessed by \_\_\_\_\_

Date

and  
 hv

to page 60

Date

12-14-8

IBM Technical Notebook

5

# $Y_1Ba_2Cu_3O_x$ Implantation Experiment

PRE - film on  $SrTiO_3$  3500/30,000

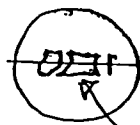
3.07  $\phi.448$  0.485 0.799 3.84 ~60.4 %



line 'MARKER' || to long axis of triangular  $SrTiO_3$  implant  
implant orientation - NOTE: MARK ON UNDERSIDE of pellet  
film side opposite

3.02 1.271 0.346 0.508 6.02 94-95

3.05 1.448 0.476 0.784 3.89 ~61



line 'MARKER' || to long cutting axis of two pellets (cut on line)  
implant orientation - see NOTE above for polished side over  
NOTE  
94-95

2.99 1.272 0.391 0.497 6.02

5

5:12 p.m. 475C @ 10C/min to 975  $\Delta 500C/10C/min = 50 min \sim 6:00 pm$

Cutting  $SrTiO_3$  implant: measures 0.5" on SAW (0.025-0.505 tangents)

$$\frac{1.272}{2.54} = 0.484 \checkmark$$

The above understood  
and witnessed by \_\_\_\_\_

Date \_\_\_\_\_

and  
by \_\_\_\_\_

Date \_\_\_\_\_

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12-21-88 Calkination III 2201-B3

X-RAY SHOWS DISTINCTLY NOT SINGLE  $\phi$ , even though material looks "OK"

total 177.04  
 curx 87.98  
 89.06 88.2

12-22-88

175.7 - (-1.34) slight sticking (RXN) w/ cur. bottom

87.98  
 87.72

89.51 (theo.) = 1.79 g greater than theoretical loss  
 could be grinding loss 2%

RE  
 850 cal

174.93 total  
 87.93 tare (after acid cleaning)  
 87. — g 0.72 g grinding loss (consistent w/ previous losses)  
 + X-ray slide

POST  
 12-22-88

174.83  
 87.93  
 86.90 -  $\Delta 0.10$  100% RXN ! nonstanc weight  
 not overconcluding but not surprising  
 batch #1 wasn't either

IBM Technical Notebook

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12-27-88

Summary various RXN pellets:

5 wt% 2201 in 0011 for 16h @ 850C SEM

5 wt% 2201 in 0011 for 2h @ 975C SEM

[0011-2201 ~~submicron mixture~~ ~~pressure-treated~~ pellet: 13h 850C } later  
1/2 Ø formation, exaggerated grain growth/warpage]

0011 @ 975C 17h SEM STD.

2201 @ 875C 1h SEM STD.

2212 @ 853C 5min SEM STD.

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Date

and  
by \_\_\_\_\_

Date



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12-29-88

Dave's Compositions

<del>#</del> Y	Ba	Cu	Y	Ba	Cu
(0.157)	(0.33)	(0.50)	0.17	0.33	0.50
0.15	0.33	0.52	0.8639	1.9038	3—
0.17	0.35	0.48	1.0625	2.1875	3—
0.19	0.33	0.48	1.1875	2.0625	3—
0.19	0.31	0.50	1.14	1.86	3—

Calculated Compositions (calculations next page)

	Y	Ba*	Cu	total	
1)	1.91937 (1.92)	6.51253 (6.51)	3.97697 (3.98)	12.48	←
2)	1.69356 (1.69)	6.51253 (6.51)	4.13605 (4.14)	12.34	←
3)	1.92	6.90723 (6.91)	3.81789 (3.82)	12.65	
4)	2.14518 (2.15)	6.51 0.33	3.82 0.48	12.48	←
5)	2.15	6.1783 (6.18) .31	3.98	12.31	←

\* Ba as BaCO<sub>3</sub>  
Y as Y<sub>2</sub>O<sub>3</sub>  
Cu as CuO

} NOTE → no purity corrections applied yet

The above understood  
and witnessed by ...

Date

and  
by

Date

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1/3/89  
Calculations for weights summarized on page 62

2)  $y_{0.15} Ba_{0.33} Co_{0.52}$

$y = 0.15 (225.8082) / 2 = 16.9356 g \quad y_{1/2} O_3$

$Ba = 0.33 (197.3494) = 65.1253 g \quad BaCO_3$

$Co = 0.52 (79.5394) = 41.3605 g \quad CoO$

3)  $y_{0.17} Ba_{0.35} Co_{0.48}$

$y = 0.17 (225.8082) / 2 = 19.1937 g \quad y_{1/2} O_3$

$Ba = 0.35 ( ) = 69.0723 g \quad BaCO_3$

$Co = 0.48 ( ) = 38.1789 g \quad CoO$

4)  $y_{0.19} Ba_{0.33} Co_{0.48}$

$y = 21.4518 \quad Ba = 65.1253 \quad Co = 38.1789$

5)  $y_{0.19} Ba_{0.31} Co_{0.50}$

$y = 21.4518 \quad Ba = 61.1783 \quad Co = 39.7697$

1)  $y_{0.17} Ba_{0.33} Co_{0.50}$

$19.1937 \quad 65.1253 \quad 39.7697$

The above understood  
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Date

and

Date

1/8/89

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1)

~~0.2~~ (TRIAL #1)  
 O<sub>2</sub> FIRED

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$2 \rightarrow 88.5409$   $\frac{1}{0.17} \text{ Ba}_{0.33} \text{ Cu}_{1.5}$

$\frac{1}{2} \text{O}_3 - 1.92$

$\text{CuO} - 3.98(1)$

$\text{BaCl}_2 = 6.51$   
 $6.588(7)$

88.53  
 tare  $\frac{76.06}{12.47}$

2.3120  
 $\frac{0.3900}{1.922}$

✓

4.3712  
 $\frac{0.3900}{3.98(12)}$

$\frac{6.9665}{6.7785} = 6.9685$   
 $\frac{0.3888}{6.5777} = 1248$

post dry  $\frac{12.43}{12.47}$

$\rightarrow 91.6\% \text{ recovery total } - \Delta = 0.05$

1-9-89

10.95 g after 2<sup>nd</sup> 16h 950C O<sub>2</sub> calcination

$6.5777 \cdot \left( \frac{153.8394}{197.3510} \right) = 5.11 - \Delta 1.47$   
 0.777

$\frac{12.43}{1.47}$   
 $\frac{12.96}{12.96}$  ✓

1/17 Dave) post 1h grind = 1.86  $\mu\text{m}$  3000/30,000

P1 1.68 1.136 0.408 0.4135 4.06 63.8%

In O<sub>2</sub> @ ~3:00 p.m. 1/10/89, to temp @ 950C projected 4:30 5:00 → 9:00

16h 1.64 1.011 0.354 0.284 5.775 90.8 (91)

1/4/88

4) ~~8~~ fired  
O<sub>2</sub>

Y<sub>0.19</sub> Ba<sub>0.33</sub> Co<sub>0.48</sub>

~~1.89~~ 6.51 ~~4.19~~  
~ 2.15 3.82

3.8217

.3865

4.2082

Y<sub>2</sub>O<sub>3</sub> =

~~2.5342~~ 6.9623 ~~4.2093~~  
~~0.3865~~ 0.384 0.3865  
2.1477 6.9783 3.8218

⇒ 12.55 g

1/10/88

Second generation started after grinding. No evidence of liq formation. Powder looks good already.

10.99 g after 2<sup>nd</sup> calcination;

10.76 post grind

~~6.58~~ (.777) = 5.11 - Δ 1.47

12.55  
- 1.47  
11.08 g expected

Recovery

1/17

P1 Pre 2500/30,000 to temp @ ~ 5:00 p.m.

1.60 1.14 0.399 0.4073 3.93 62% ✓

1/18

1.58 1.055 + 0.365 0.319 4.95 77.8%

Green φ peaks coming up in X-ray.

66

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5) 4.19 Ba 0.31 Co 0.50  
 (.99)  $\frac{1}{2}O_3 - 2.44(13)$   $\frac{2.976}{.99} \rightarrow 6.17(96)$   $\frac{6.4690}{.99} \rightarrow 6.2407$   $CO - 3.9810$   $\frac{4.2092}{.99} \rightarrow 4.2527$   
 $\frac{2.3761}{0.2287} = 2.1474$   $\frac{6.4690}{0.2289} = 6.2411$   $\frac{4.2092}{0.2282} = 12.37$   
 $3.9810 \Rightarrow 12.3695$

12.34(3) collected after mix // 12.34/12.37  $\sim \Delta 0.24\%$  ✓

$6.2411 - 4.8493 = 1.392$

$\frac{63.50}{51.17} = 12.33$   $\frac{62.20}{51.17} = 11.03$   $\Delta 1.3/1.39 = 93.5\%$

11.00 post GRND  $\frac{62.17}{51.18} = 10.99$  post CA II 62.11  $\frac{11.63}{10.75}$

Post GRND 10.46  
 PRE  $\frac{9333}{30,000}$   
 1.60 1.440 0.244 0.40 4.00 62.9  
 Post 1.56 1.266 0.210 0.267 6.00 (94-91)

Good densification, no apparent liq, CO islands present,

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Date

and by

Date

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2201

P1B3 2500/30000  
PRE 1.94 1.09 0.391 0.365 5.315 73.8%  
Post 15 min @ 860  
1.94 1.06 0.359 0.313 6.2 86%

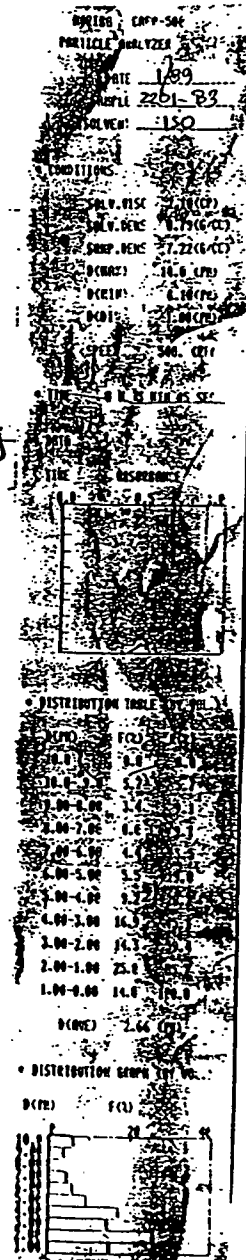
2 wt % 2201 in 0011 1/13/88

9.49  
0.19  
9.58  
some leaking during 8.5h mix : 9.05 g  
9.05 g  
8.68 g Small  
0.37 g loss  
8.68 g  
0.37 g

2 wt % P1 4200/30,000 to temp @ ~5:00 p.m.  
Pre 1.70 1.163 0.499 0.53 3.21 ~64.2  
1.69 1.21 0.525 0.60 2.82 56.4  
1.194-1.227  
same slumping  
-Δ 12%

Cuts yield : 1.57 mm inside 0.30  
1.12 mm center 0.25  
polished → 1.79 mm outside 0.380 (two)

+ 26.52 26.03 25.94  
post 25.52 25.52 25.45  
1.00 → 1000 μm 490  
570



The above understood  
and witnessed by \_\_\_\_\_

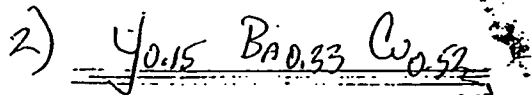
Date

and

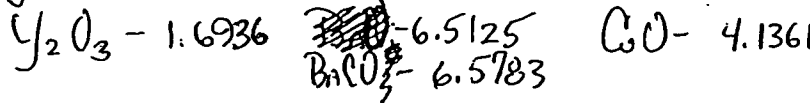
Date

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IBM Technical Notebook



bottle ton: 74.55



(.22705)	$\frac{1.9206}{\underline{0.2288}}$	$\frac{6.8066}{\underline{0.2284(8)}}$	$\frac{4.3651}{\underline{0.2288}}$	<u>total</u>
	$\sim 1.6936$	$6.5782$	$4.1363$	$(0.22705) \sim 12.41$

1/17 1<sup>st</sup> calcination

tone  $\frac{66.53}{54.16}$  (12.37 measured from weighing)  
 $\frac{54.16}{12.37} \checkmark / 12.41 = -\Delta 0.3\%$

$6.5783(.277) = 5.111 (-1.47)$   $\frac{12.37}{-1.47}$   
 $\sim 10.90$  expected yield (less transfer losses)

1/18 post  $\frac{66.53}{65.15(05)}$  tone 54.20 recovery  $\frac{65.05}{54.2}$   
 $- \Delta \frac{1.38(48)}{10.85}$   $\sim$  total rxn.

2<sup>nd</sup> CAL (16h as above)

1/19 POST  $\frac{65.02}{54.2}$   
 $\frac{54.2}{10.82} \checkmark \sim$  constant 10.79 recovery

Notes: large liq stains (formation) during 1<sup>st</sup>/2<sup>nd</sup> cal unlike

PRE P1 1 & 4 where liq was suppressed in 1<sup>st</sup> cal { minor in 2<sup>nd</sup> }  
 $\frac{3380}{30,000}$  75C @ 5:16 p.m. temp @ 7:45, 16h  $\rightarrow$  11:45 A.M.  
 6:40 p.m.

1.60 1.414 0.258 0.405 3.95 62.1%

1.57 1.227 0.216 0.255 6.16 96.9

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1)  $O_2$

4)  $O_2$

2)  $O_2$

3)  $O_2$  1h iso

PSD's  
5)  $O_2$

MODEL CPM-500  
PARTICLE ANALYZER

DATE 1-10-89  
SAMPLE Y. B. 33 C. 05  
SOLVENT ISO-1h

• CONDITIONS

SOLV. VISC 2.10 (CP)  
SOLV. DENS 0.75 (G/CC)  
SAMP. DENS 6.36 (G/CC)  
D(CORR) 10.0 (CP)  
D(CORR) 0.10 (CP)  
D(CORR) 1.00 (CP)  
SPEED 500 (RPM)

• TIME 0.0 4 MIN 20 SEC

• DATE

TIME ABSORBANCE

• DISTRIBUTION TABLE (BY VOL.)

D(CP)	F(C)	R(C)
10.0-9.0	0.0	0.0
9.0-8.0	1.2	1.2
8.0-7.0	2.3	4.1
7.0-6.0	0.0	4.1
6.0-5.0	0.0	4.1
5.0-4.0	5.5	5.6
4.0-3.0	13.2	25.5
3.0-2.0	16.5	46.8
2.0-1.0	26.9	74.5
1.0-0.0	25.1	100.0

D(CORR) 1.00 (CP)

• DISTRIBUTION GRAPH (BY VOL.)

MODEL CPM-500  
PARTICLE ANALYZER

DATE 1-13-88  
SAMPLE Y. B. 33 C. 05  
SOLVENT ISO

• CONDITIONS

SOLV. VISC 2.10 (CP)  
SOLV. DENS 0.75 (G/CC)  
SAMP. DENS 6.36 (G/CC)  
D(CORR) 10.0 (CP)  
D(CORR) 0.10 (CP)  
D(CORR) 1.00 (CP)  
SPEED 500 (RPM)

• TIME 0.0 4 MIN 20 SEC

• DATE 07

TIME ABSORBANCE

• DISTRIBUTION TABLE (BY VOL.)

D(CP)	F(C)	R(C)
10.0-9.0	0.0	0.0
9.0-8.0	1.2	1.2
8.0-7.0	0.0	0.1
7.0-6.0	0.0	0.1
6.0-5.0	0.0	0.1
5.0-4.0	5.5	13.2
4.0-3.0	13.2	26.5
3.0-2.0	11.4	36.8
2.0-1.0	29.6	67.6
1.0-0.0	22.2	100.0

D(CORR) 1.00 (CP)

• DISTRIBUTION GRAPH (BY VOL.)

MODEL CPM-500  
PARTICLE ANALYZER

DATE 1-20-89  
SAMPLE Y. B. 33 C. 05  
SOLVENT ISO

• CONDITIONS D-0.8

SOLV. VISC 2.10 (CP)  
SOLV. DENS 0.75 (G/CC)  
SAMP. DENS 6.36 (G/CC)  
D(CORR) 10.0 (CP)  
D(CORR) 0.10 (CP)  
D(CORR) 1.00 (CP)  
SPEED 500 (RPM)

• TIME 0.0 4 MIN 20 SEC

• DATE

TIME ABSORBANCE

• DISTRIBUTION TABLE (BY VOL.)

D(CP)	F(C)	R(C)
10.0-9.0	0.0	0.0
9.0-8.0	5.4	5.4
8.0-7.0	0.0	5.4
7.0-6.0	0.0	5.4
6.0-5.0	2.3	7.7
5.0-4.0	3.8	11.4
4.0-3.0	12.2	23.6
3.0-2.0	16.2	40.8
2.0-1.0	16.3	56.3
1.0-0.0	36.6	86.5
0.0-0.0	15.1	100.0

D(CORR) 2.30 (CP)

• DISTRIBUTION GRAPH (BY VOL.)

MODEL CPM-500  
PARTICLE ANALYZER

DATE 1-27-89  
SAMPLE Y. B. 33 C. 05  
SOLVENT ISO

• CONDITIONS D-9.6

SOLV. VISC 2.10 (CP)  
SOLV. DENS 0.75 (G/CC)  
SAMP. DENS 6.36 (G/CC)  
D(CORR) 10.0 (CP)  
D(CORR) 0.10 (CP)  
D(CORR) 1.00 (CP)  
SPEED 500 (RPM)

• TIME 0.0 4 MIN 20 SEC

• DATE

TIME ABSORBANCE

• DISTRIBUTION TABLE (BY VOL.)

D(CP)	F(C)	R(C)
10.0-9.0	0.0	0.0
9.0-8.0	1.0	1.0
8.0-7.0	0.0	1.0
7.0-6.0	0.0	1.0
6.0-5.0	0.0	1.0
5.0-4.0	1.0	2.0
4.0-3.0	11.0	13.0
3.0-2.0	14.0	24.0
2.0-1.0	20.0	44.0
1.0-0.0	23.0	67.0

D(CORR) 1.00 (CP)

• DISTRIBUTION GRAPH (BY VOL.)

MODEL CPM-500  
PARTICLE ANALYZER

DATE 1-24-89  
SAMPLE Y. B. 33 C. 05  
SOLVENT ISO

• CONDITIONS

SOLV. VISC 2.10 (CP)  
SOLV. DENS 0.75 (G/CC)  
SAMP. DENS 6.36 (G/CC)  
D(CORR) 10.0 (CP)  
D(CORR) 0.10 (CP)  
D(CORR) 1.00 (CP)  
SPEED 500 (RPM)

• TIME 0.0 4 MIN 20 SEC

• DATE

TIME ABSORBANCE

• DISTRIBUTION TABLE (BY VOL.)

D(CP)	F(C)	R(C)
10.0-9.0	0.0	0.0
9.0-8.0	0.0	0.0
8.0-7.0	0.0	0.0
7.0-6.0	0.0	0.0
6.0-5.0	0.0	0.0
5.0-4.0	0.0	0.0
4.0-3.0	0.0	0.0
3.0-2.0	0.0	0.0
2.0-1.0	0.0	0.0
1.0-0.0	0.0	0.0

D(CORR) 1.00 (CP)

• DISTRIBUTION GRAPH (BY VOL.)

The above understood  
and witnessed by

Date

and

Date



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IBM Technical Notebook

$$\begin{array}{lcl}
 S_{r7} C_{12} D \rightarrow S_{0.37} C_{0.63} D_{19} & S_{rD} & C_{10} \\
 38.34 & 50.1078 & \\
 S_{rC} D \rightarrow S_{0.5} C_{0.5} D_7 & 51.8077 & 39.7697 \\
 S_{rC} D \rightarrow S_{0.67} C_{0.33} D_3 & 69.4250 & 26.248 \\
 S_{rD} = 103.6194 \rightarrow S_{rD}_3 & 112.63 & 142.47 \\
 C_{10} = 79.5394 & & \\
 3.83 & 5.02 & \\
 3.834 & 5.0198 & \rightarrow 8.8538 \\
 (5.11) 5.18077 & 3.97897 & (5.78) \rightarrow 9.1579 \\
 (6.29) 6.9425 & 26.248 & (6.63) \rightarrow 9.5673 \\
 \downarrow & \downarrow & \\
 5.46 & 5.02 & 10.48 \\
 7.34 & 3.98 & 11.36 \\
 9.89 & 26.24 & 12.52 \\
 S_{rD}_3 & C_{10} &
 \end{array}$$

The above understood

Date

and

Date

1/17/89

CO11-5 at 201 @ 8500 for attempted TCM prep.

slice 2 - 1.28 mm - 1280  $\mu$ m

slice 3 - 0.68 680  $\mu$ m

slice 2 prep: mounted side 1 measures ~ 27.64  
12.80  
26.30 - (3.5)  
1.34 - 1.29

am: 300  $\mu$  1340  
980/2 = 490 - 490

20 8's on "soft" 15  $\mu$ m yields ~ 900 { 150 8's on 6 give 770  
850 target  
720  $\mu$ m before starting second side

26.40 after mount 30  $\rightarrow$  26.21  
25.69 25.49  
0.71 520

150  $\rightarrow$  26.16  
1430

150  $\rightarrow$  26.06  
330

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IBM Technical Notebook

3)  $O_2$  fixed

$Y_{O_2} = 0.17$   $Bu = 0.35$   $Co = 0.48$

$Y_{O_2} = 1.9213$

$BuCO_2 = 6.9770$

$CO = 3.8217$

$2.1495$   
 $0.2288$   
 $1.9212$

$7.2050$   
 $0.2277$   
 $6.9773$   
 $5.4214$

$4.0499$   
 $0.2281$   
 $3.8218$

Some bumping, but very good mix as should be true. 12.35 post mix

12.72 of expected REDO (Bumping too critical)

$Y_{O_2} = 1.9213$

$BuCO_2 = 6.9770$

$CO = 3.8217$

$2.1425$   
 $0.2240$   
 $1.9215$

$7.1973$   
 $0.2200$   
 $6.9773$

$4.0428$   
 $0.2210$   
 $3.8218$   
12.72

Mix recovery after accurate drying:  $12.63/12.72 = \Delta 0.7\%$  (acceptable)

$63.82$   
 $51.19$

Post  $62.35$   
 $51.20$   
 $11.19$

Cal #I: 3:57 1900 w 5:15 est temp attainment  
4:25 486C ~ seems correct

(11.17 expected)  
Post cal II

Post grind I: 11.21  $\rightarrow$  11.14 62.35

$62.24$   
 $51.20$   
 $11.05$

Very little liq formation compared to #2. Apparently need excess Bu and Co for larger liq.

0.2 g loss due to Si carbon from tube (pre-grow) 10.8

The above understood

Date

and

Date

1/27

IBM Technical Notebook

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10.97 collected: white top layer on powder. Dry flake-cake  
very agglomerated/brittle and does not easily pick out when  
brushed. Had to dry grind in order to produce decent prod.

10.25 recovered for dry grind

P1 3500/29000

1.62 1.425 0.266 0.424 3.82 60—%

1.52 1.321 0.245 0.336 4.52 71 %

Pre grind & Post grind x-rays show change of some peaks  
in two x-rays, however sintering calculation of pellet may  
refer to products to original  $\phi$ 's. Will do x-ray of pellet

also.  
Post: some slumping.

The above understood  
and witnessed by \_\_\_\_\_

Date \_\_\_\_\_

and  
by \_\_\_\_\_

Date \_\_\_\_\_

74. 4/10/87 125 Variation Study IBM Technical Notebook

Property Pellets

#1 P2 3.000/50,000

ave = 62.5

1.04	1.138	0.256	0.260	4	62.3
1.01	1.046	.22	0.187	5.34	84

#2 P2

1.02	1.123	0.264	0.261(5)	9.90	67.3
------	-------	-------	----------	------	------

1.00	9.87	.22	0.168(6)	5.75	93.6
------	------	-----	----------	------	------

#3 P2

1.04	1.154	0.248	0.258	4.03	63.4
------	-------	-------	-------	------	------

1.024	1.024	.224	0.184	5.54	87
-------	-------	------	-------	------	----

Pellets in Furnace @ ~10:30 A.M. 2/17/87 10°/min (pre-warmed)

10:30	259	239	(?)
10:45	442	518	+Δ 75.75
11:50	900.5p	944	

non early exits. P@ 300 went down by 25. too estimated time to reach stop point would be 45 mins. at 11:30 @ +Δ 50 pre-warmed or 95°C then relaxation over ensuing 20 mins. of 6°C. Delay in pulling run requires extra time as BC is probably close. project over 2 hrs. 1:45 Mon.

1:45 PM 2/17/87

Furnace @ 600C

project over 2 hrs. 1:45 Mon.

see page 145

2/6/89

IBM Technical Notebook

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Experiments to look at  
Carbonate in 123

clean gas with ascorbic

Sample 1: dense closed  
porosity, 0.791%

cut sections from center

Sample 2: open porosity  
0.87%

center sections

thin slices on aggregate

(2) 3 pellets of each (Peter)  
center sections of each

(1) T am / EELSS (P. Burton)

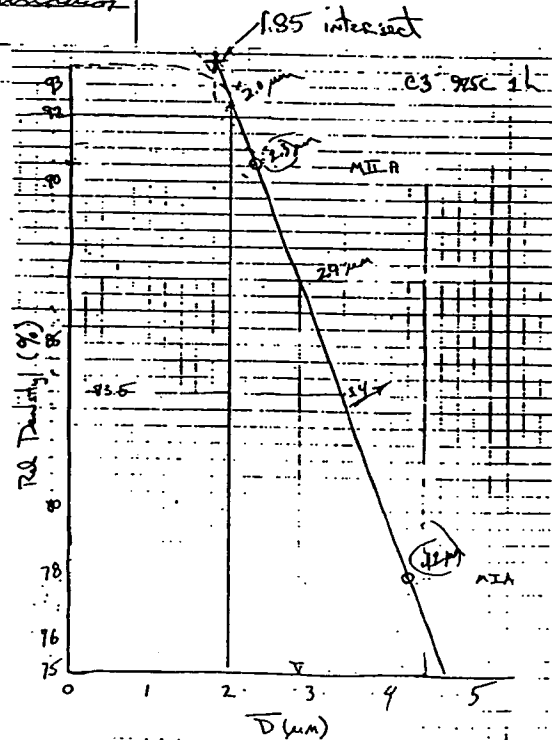
(2) Magnetometer (T. Maguire)

(3) Induction (Diane Davis)

(4) CO<sub>2</sub> evolution on dissolution

(5) X-ray lattice

(6) XPS



The above understood

Date

and  
by

Date

[illegible]

Date \_\_\_\_\_

2/7/89

IBM Technical Notebook

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PI mill  $D = 4.21 \mu m$  (guide)  
3333/28500

Pre wght: 3.46 (of 3.5) some deformation during iso pressing, but slight  
Post 975C 1h minimal so hardness can be reduced.

3.41 1.402 0.448 0.69 4.94 77.7  $\rightarrow$  78% 4.2 too low

PII mill  $D = 2.34 \mu m$  (slow)

PRE 3900/29000

3.46 1.453 0.543 0.9 3.84 60.5 reasonable

3.40 1.285 0.456 0.59 5.76 90.6  $\langle$  NEED SLIGHTLY HIGHER  $\rangle$

Tomorrow  $\rightarrow$  will mill in

for

Yields: PRE MI : 48g

gap B

gap A { 24 MIIA: 20g  
16 MIIA: #

20.5



error in pre-weights

78 M4A  $\bar{D} = 1.85$  PRE - 4000/30,000 20/mw to 675 10/mw to 975  
 P3  $\textcircled{3.40}$  1.452 0.543 0.9 3.78 59.4 } given  
~~3.38~~  
 3.48 1.265 0.460 0.578 6.02 94.6 next

P4  $\textcircled{3.41}$  1.462 0.540 0.91 3.75 59. -  
 3.60 1.274 0.468 0.596 6.04 95 - heavy

P5  $\textcircled{3.93}^+$  1.457 0.561 0.935 3.67 57.7<sup>+</sup>  $\rightarrow \geq 58$   
 3.60 1.280 0.482 0.62 5.81 91.4<sup>+</sup>  
 3.65 5.89 92.6 } Probably even higher

MIFB - 4000/30,000 80  $\mu$ m

P6  $\textcircled{3.55}$  1.463 0.508 0.85 4.17 65.6  
 3.53 1.35 0.484 0.674 5.24  $\textcircled{82.4}$  next

P7  $\textcircled{3.54}$  1.462 0.504 0.85 4.165 65.5  
 3.59 1.358 0.462 0.668 5.36  $\textcircled{84.5}$  heavy

P8  $\textcircled{3.56}$  1.463 0.507 0.85 4.19 65.9  
 3.73 1.352 0.453 0.65 5.73 90.2

\* laminated on 1 side, not severe (must be 'repelletized' pellet)

P9 4000/30000

3.57 1.462 0.517 0.87 4.1 64.5

3.56 1.354 0.463 0.666 5.35 84.2

P10 fines 4/3 as above

1.53 1.436 0.254 0.411 3.72 58.5 was expected

1.54 1.254 0.207 0.256 6.02 94.7 { doesn't look good

Pellet cutting NEXT (see pg 80 for plan overview)

Pellet 3 1/4 dedicated to vertical & horiz. slicing

Pellets 6 & 7 ↓ ↓ ↓ ↓ ↓

from tangent saw cut edge: 1 mm slices are 0.055" w/ blade

Low Density Vertical slices: 1 1.2 slices } 7 altogether + one piece  
6 1.0 slices } and polished end (unusable)

Horizontal: 2 1.0 slices mid section  
1 0.5 top  
1 1.0 bottom

High Density

vertical: 5 slices (and lost to chipping) lead polished  
~2mm ← 1 polished thick chunk  
~1.2mm { 3 oxygenated  
1 SAs  
horiz: 2 mid section  
1 ea top & bottom (top chipped)

28/8/89  
Oxygenation Diagram { scheme

LD marker (and piece)

specimens tilted on clean  $Al_2O_3$  surface

HD LD

$O_2$  flow

To 600C @ 1:30 p.m. 2/15/89 in dry,  $\text{CO}_2$ -free  $\text{O}_2$ .

1 mm vertical slices

10 min to 850°C, 10 min to 600 °C  
(48h), quench.

- 1) 1 slice for Jacarj Bews (Ramon)
- 2) 1 slice for Alex for XPS of fracture surface
- 3) save remainder for future use (classified)
- 2A) 1 extra slice originated

inner horizontal slices 4 of outer slices discarded

- 1) 1 slice (10mm) goes to a 5mm cut 3 3mm discs w/  
ultrasonic in isopropanol de. (if possible).  
1 disc to Tom  
2 discs for TEM  
1 spare

- 2) 1 slice dedicated to  $\gamma$  vs  $T$  to Drane's spec

Pellet (3) O/C

space for (1) x-ray lattice  
(2) CD evolution

2/16/89

A1

## C4 Synthesis Preparation/Notes (ref book IV, pg 46 &amp; pg 14)

	oxide wt. frac.	atomic % $\frac{1}{2} \text{Ba}, \frac{1}{2} \text{C}$	oxide M.W.
$\frac{1}{2} \text{O}_3$	0.1751	.17	225.81
BaO	0.4651	.33	153.34

CO : 0.3625 ~ .5 79.54

Go with the new

Example Calc: wt frac deriv

	oxide wt. frac
$\frac{1}{2} \text{O}_3$ 225.81 g $\times \frac{.17 \text{ mole}}{1 \text{ mole}} = \frac{38.39}{2} = 19.19$ $19.19/109.56 = 0.1751$	
BaO 153.34 $\times .33 = 50.60$ $50.6/109.56 = 0.4618(5)$	
CO 79.54 $\times .5 = 39.77$ $39.77/109.56 = 0.363$	
	0.9999

17.51 g  $\frac{1}{2} \text{O}_3$ 

1.287009

46.18 g BaO

$$\left\{ \begin{array}{l} 197.35 \times 46.18 \\ 153.34 \end{array} \right\} 59.43 \text{ g BaCO}_3$$
 $\frac{1}{2} \text{O}_3$ 19.19/.99 = 19.209  $\rightarrow$  19.21  $\approx \times 1.5$  28.81(5) 28.82BaCO<sub>3</sub>50.60(2)  $\times \left( \frac{197.35}{153.34} \right) = 65.12(5)$  97.69

CO

39.77/.99 = 39.87 59.71(5) 59.72

97.69 (0.1777) = 75.91 - 97.69 =

186.23

- 21.78

164.45

CO<sub>2</sub>

A2

Administrative Notes

# FINAL Batch Size for REASONABLE BULK HANDLING

$$\frac{1}{2}O_2 \quad 17.51 / .999 = 17.52(7) \approx 17.53$$

$$BaCO_3 \quad 65.12(5) / .9999 = 65.12(5) \approx 65.13 \quad \rightarrow 343.78$$

$$CO \quad 39.77 / .999 = 39.80(9) \approx 39.81$$

$$122.47$$

$$\begin{array}{r} 343.78(7) \\ \text{tare } 278.65 \\ \hline 65.13 \end{array} \quad BaCO_3 \quad \frac{1}{2}O_2 \quad 17.53 \quad \text{weighed/transformed}$$

(A.O. 0.01?)

$$\begin{array}{r} 382.76 \\ \text{t } 343.78(7) \\ \hline 39.98 \end{array} \quad CO \quad \text{Mixing yield} \quad \begin{array}{r} 122.29 \\ \hline 122.47 \end{array} \quad \begin{array}{r} 99.85\% \\ -10.15 \end{array}$$

(A.O. 0.03)

$$\begin{array}{r} 151.42 \text{ OK} \\ \text{tare 1 } 37.49 \\ \hline 113.93 \end{array} \quad \begin{array}{r} 140.48 \\ \text{tare 2 } 82.12 \\ \hline 58.36 \end{array} \quad \rightarrow X \text{ bad hunt dimensions}$$

$58.36 = 122.29$

$$\begin{array}{r} 146.97(6) \\ 88.61 \\ \hline 58.36 \end{array} \quad \swarrow \text{sintered much more / some lca form}$$

$$\begin{array}{r} 151.42 \\ \text{tare 1 } 144.37 \\ \hline 7.05 \\ 87.55 \end{array} \quad \begin{array}{r} 146.97 \\ \text{tare 2 } 141.74 \\ \hline 5.23 \\ 88.64 \end{array} \quad \swarrow \text{less sintered, less lca}$$

$-12.28 \text{ (O}_2 \text{ loss vs expected)}$   
 $14.53 \text{ expected}$   
 $(105\% \text{ reached})$   
 $2.25 \text{ to go}$

after gross  $108.71 / 110 = 98.8\% -1.2\%$

$$\begin{array}{r} 197.383(2) \\ 88.64 \\ \hline 108.74 \end{array}$$

	$\gamma/\text{Al}_2\text{O}_3$	$\text{BaCO}_3$	$\text{CaO}$	SLS / Result
C4-1	0.17	0.33	0.5	assumed stone pure
	0.16	0.36	0.5	analytical determination

C4-2	0.17	0.33	0.5	analytical <u>lit</u>
------	------	------	-----	-----------------------

$\Delta$	+0.01	-0.03	-
----------	-------	-------	---

C4-3	0.16	0.35	0.5	analytical
------	------	------	-----	------------

$\Delta$	-0.01	+0.02	-
----------	-------	-------	---

$\Delta_{\text{net}}$	-	-0.01	-
-----------------------	---	-------	---

-3E	0.165	0.35	0.5
-----	-------	------	-----

$\Delta$	-0.005	+0.02	-
----------	--------	-------	---

$\Delta_{\text{net}}$	+0.005	-0.01	-
-----------------------	--------	-------	---

C4-4	0.16	0.34	0.5	analytical
------	------	------	-----	------------

$\Delta$	-	-0.01	-
----------	---	-------	---

$\Delta_{\text{net}}$	-	-0.02	-
-----------------------	---	-------	---

C4-5	0.16	0.34	0.49	analytical
------	------	------	------	------------

$\Delta$	-	-	-0.01
----------	---	---	-------

$\Delta_{\text{net}}$	-	-0.02	-0.01
-----------------------	---	-------	-------

Species  
Implication  $\rightarrow$  trace content,

C4-6	0.16	0.34	0.478	$\text{CuO} \rightarrow \text{Cu}_2\text{O}$
------	------	------	-------	--

$\Delta$	-	-	-0.022
----------	---	---	--------

$\text{BaCO}_3 \rightarrow \text{Ba(OH)}_2$

$\Delta_{\text{net}}$	-	-0.02	-0.03
-----------------------	---	-------	-------

$\gamma_2\text{O}_3 \rightarrow \gamma_2\text{O}_3 \underline{\underline{X}}$

C4-7	0.16	0.34	0.478
------	------	------	-------

$\Delta$	-	-	+0.008
----------	---	---	--------

$\Delta_{\text{net}}$	-	-0.02	-0.022 $\uparrow$
-----------------------	---	-------	-------------------

# C4-7 TRANSFORM TO STOIC basis

$\frac{1}{2}O_2$	$Ba(OH)_2$	$Cu(OH)_2$	
0.17	0.31	<del>0.498</del>	0.48

Correct for fuel batched

$\frac{1}{2}O_2$  is good as received

$BaCO_3$  is Barium rich by 0.02 at%

$CuO$  is Copper rich by 0.02 at%

A3

Administrative Notes

Post: CA II in 60 hrs @ 950C in  $O_2$ 

3/27

195.52  $\rightarrow$  post 88.94 (22g rxn)

88.64

 $106.88 - 108.69 = 1.81 / 2.25 = 80.5\%$  of remainder $\frac{12.28}{14.09 / 14.53 \text{ theo.}} = 97\% \uparrow$  lessMinimal  $Li_2$  formation.

99.57g yield (due to contamination)

{ further contamination upon re-submission to the for cal<sup>th</sup> reduces yield furtherPeaks @ ~30.2, 29.4, 28.5  $2\theta$  Dunsberg. May be  $BiCl_3$ , but could also be  $2\theta$ 

$$n\lambda = 2d \sin \theta \Rightarrow d = \frac{\lambda}{2 \sin \theta} \quad 100 = 3.72$$

something wrong here

$$3.72 = \frac{\lambda}{2 \sin \theta}$$

$$4.803 = \sin^2 \theta$$

4/19

From Hechtly:  $1.96 Ba_{2.16} Cu_3$  ( $1.72 Ba_{2.72} Cu_1$ )  $O_{2.2}$ In reference to VARIATIONAL study:  $\frac{0.116 \pm 0.01}{\pm 0.005} \frac{0.36}{0.5} = 1.02$





2/17/89 page 4

975C Property Pellet for information study - On 2 g pellets should give enough material for 4.4 mm thick sintered body allowing a slice to be cut up an interior & exterior surface.

7.5 g #1 stock 1.92 used for pellet (.17 .33 .5)

7.6 g #2 stock 1.90 ↓ (.15 .33 .52)

8.5 g #3 stock . . . (17.35.48)

9 #4

2.7 #5 to 600C @ 20/min; 10 min to 975C 4131-625C  
3600/29,000 Quench 1h -510

#1 P3

1.92	1.144	0.479	0.489	3.93	61.8
1.90	1.0	0.4	0.314	6.05	95-

#2 P3

1.91	1.126	0.490	0.488	3.91	61.5
1.88(?)	0.98	0.412	0.311	6.045	95-

#3 P3

1.95	1.133	0.503	0.507	3.85	60.5
1.85	0.998	0.43	0.336	5.51	86.6

#4 P2

1.90	1.139	0.481	0.490	3.88	61-
1.86	1.05	0.43	0.37	5.03	79-

#5 P3

1.87	1.145	0.46	0.474	3.99	62.7
1.86	0.993	0.388	0.300	6.2	97.5
	1.05	0.41			

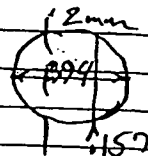
#1-5

Pellets showing oxygenation @ 600C for 66 hrs in D<sub>2</sub>

0.394 inches

0.157 in for center cut

-0.08 - 2 mm



#1 PL1 Pre 63.5%

Post 1.85 1.025 0.406 0.335 5.52 87

## 2/28 Property Pellet Summary (to date)

	cube	1g	X	X	CO	REA#
	#1	#2	#3	#4	#5	
oxygenated	975 (95)	95	(87)	(79)	975	R3
no structure 2/28	950 II' (84)	(94)	-	-	(87)	R2
	950 87	Roane				R4
micro structures	orig 950	91	'97'	71	78	92
						Davis

 950 II' #1 & #5 pellets to temp @ 600C then 10C/min Ramp @ 6:15 pm  
 > oxygenation run  
 Out 10:00 A.M. 3/2 40 h D<sub>2</sub>

$$5 \text{ cc} \times \frac{6.36 \text{ g}}{\text{cc}} = 31.8 \text{ g}$$

$$\frac{\pi (2.54)^2}{4} X = 5 \text{ cc}$$

$$5.07 \text{ cm}^2 X = 5 \text{ cc}$$

$$X = 5 \text{ cm}^3 / 5.07 \text{ cm}^2$$

$$X \approx 1 \text{ cm} \text{ or } 1/2 \text{ inch} - 1 \text{ inch with shewage}$$

4/24/89

#1 - C3 wt% Cu 28.7

wt% holes 36.0

Hole Concentration Conversion Formula:

Data: wt% Cu (total): 28.7

wt% holes: 36.0

$$\frac{\text{wt\% holes} - \text{wt\% Cu}_{\text{tot}}}{\text{Cu}_{\text{tot}}} = \frac{36 - 28.7}{28.7} = 0.254$$

average 'over'  
valence

∴ add Cu valence (2) = 2.25 = average valence Cu

$$2.25 (\text{Cu}_{\text{tot}}) = 2.25 (3) = 6.75 \text{ total Cu val}$$

↑  
from sample

$$4 \text{ Ba}_2 \text{Cu}_3 \xrightarrow{2.25} 13.75$$

total Ba + Y val  
+ 7.00  
13.75

total charges

Take total charges & divide by two for  $\text{O}^{2-}$ 

$$13.75/2 = 6.88 \text{ atoms} \Rightarrow \text{YBa}_2\text{Cu}_3 \text{O}_{6.88}$$

2.25

see  
page after  
next

## Notes to Kristy concerning Pellet Forming precalculations

To estimate pellet <sup>weight</sup> <sub>pack</sub> for pellet pressing:

A. take dia & approx. height desired

1. calculate volume in cc.  $(1.22 \text{ cm})^2 \cdot 0.35 \text{ cm} \cdot \pi = 0.41 \text{ cc}$

B. Assume some reasonable 'green' density (unfired, pressed pellet)

0.6-0.8 (60-80%) usual. for metals > 0.70 w/ small

ave. part. dias. (ie. 3 mm).

$\frac{0.41 \text{ cc}}{0.8} \times 9.0 \frac{\text{g}}{\text{cc}} \approx 3 \text{ g of pack.}$  ← density theoretical

I pressed @ between 16,000 & 20,000 psi.

low side for pure metal  $\therefore$

$\frac{X}{(\text{dia})^2} = \text{desired pressure}$  where  $X = 1^{\text{st}} \text{ scale pressure}$

$X \approx 4,000 \text{ for } 0.48'' \text{ dia. die.}$

K-46

K-112

MODEL: RPE-500  
PARTICLE ANALYZER  
DATE: 3/1/89  
SAMPLE: A-1  
SOLVENT: ISO

• CONDITIONS  
SOLV. VISC: 2.10 (CP)  
SOLV. DENS: 0.7916 (G/CC)  
SAMP. DENS: 2.6116 (G/CC)  
D(CHE): 10.0 (FR)  
D(CHE): 0.10 (FR)  
D(CHE): 1.00 (FR)  
SPEED: 500 (RPM)

• TIME: 13 MIN 27 SEC

DATA: 0.95

TIME: 0.0 0.5 1.0

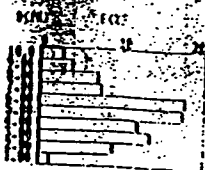


• DISTRIBUTION TABLE (BY VOL.)

D(CHE)	F(1)	F(2)
10.0-9.0	0.5	0.5
9.0-8.0	2.0	11.3
8.0-7.0	3.0	15.1
7.0-6.0	7.0	22.1
6.0-5.0	7.4	29.6
5.0-4.0	17.6	47.2
4.0-3.0	7.2	64.2
3.0-2.0	11.0	76.1
2.0-1.0	23.4	87.6
1.0-0.0	9.6	98.7
0.0-0.0	1.2	100.0

D(CHE): 4.84 (FR)

• DISTRIBUTION GRAPH (BY VOL.)



MODEL: RPE-500  
PARTICLE ANALYZER  
DATE: 3/14/89  
SAMPLE: A-2  
SOLVENT: ISO

• CONDITIONS  
SOLV. VISC: 2.10 (CP)  
SOLV. DENS: 0.7916 (G/CC)  
SAMP. DENS: 3.9716 (G/CC)  
D(CHE): 10.0 (FR)  
D(CHE): 0.10 (FR)  
D(CHE): 1.00 (FR)  
SPEED: 500 (RPM)

• TIME: 8 MIN 36 SEC

DATA: 0.9

TIME: 0.0 0.5 1.0

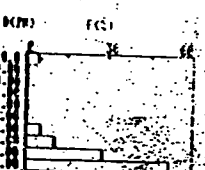


• DISTRIBUTION TABLE (BY VOL.)

D(CHE)	F(1)	F(2)
10.0-9.0	0.0	0.0
9.0-8.0	4.5	4.5
8.0-7.0	0.0	4.5
7.0-6.0	0.0	4.5
6.0-5.0	0.0	4.5
5.0-4.0	0.0	4.5
4.0-3.0	5.5	10.0
3.0-2.0	10.5	20.0
2.0-1.0	20.0	40.5
1.0-0.0	51.5	100.0

D(CHE): 0.97 (FR)

• DISTRIBUTION GRAPH (BY VOL.)



Administrative Note

9/1/07  
Analytical Results for C<sub>3</sub> H<sub>2</sub>/LD STUDY - Hole

IBM

IBM  
RESEARCH CENTER

ANALYTICAL  
LABORATORY

Request for Analysis

Use Ball Point Pen

REQUESTOR <u>T. S. Kien</u>	PROJECT NO.	REQUEST NO.																								
DEPARTMENT	LOCATION	ROOM <u>25-225</u>																								
REQUESTOR'S SAMPLE IDENTIFICATION <u>H0 ex</u>	<u>L.Dox</u>																									
APPROXIMATE COMPOSITION AND HISTORY OF SAMPLE <u>Y<sub>2</sub>O<sub>3</sub> Cu Oxide</u>																										
ANALYSES REQUESTED																										
ANALYSIS METHOD																										
<p><u>Cu</u></p> <p style="text-align: center;"><b>ANALYTICAL RESULTS</b></p> <table border="1"> <thead> <tr> <th></th> <th>H0</th> <th>LD</th> </tr> </thead> <tbody> <tr> <td>Wt% Holes</td> <td>33.5</td> <td>34.2</td> </tr> <tr> <td>Wt% Cu</td> <td>(23.5)</td> <td>27.6</td> </tr> <tr> <td></td> <td>2.21</td> <td>2.26</td> </tr> <tr> <td></td> <td>6.81</td> <td>4.689</td> </tr> <tr> <td colspan="3" style="text-align: center;"> <math display="block">\frac{\text{Total Cu} - \%}{\% \text{ Cu}}</math> </td> </tr> <tr> <td>After Reox: H0 ex</td> <td>28.7</td> <td>Wt% Cu ← 2.86</td> </tr> <tr> <td>pure at 500C</td> <td>36</td> <td>holes</td> </tr> </tbody> </table>				H0	LD	Wt% Holes	33.5	34.2	Wt% Cu	(23.5)	27.6		2.21	2.26		6.81	4.689	$\frac{\text{Total Cu} - \%}{\% \text{ Cu}}$			After Reox: H0 ex	28.7	Wt% Cu ← 2.86	pure at 500C	36	holes
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pure at 500C	36	holes																								
DATE SUBMITTED <u>9/1/07</u>	DATE REPORTED <u>9/26/07</u>	NOTES/REFERENCE <u>4/11/07 p. 121</u>																								
ANALYST <u>T. S. Kien</u>	APPROVAL																									

No



Notes to Kristy concerning ~~the~~ FORMING precalculations

To estimate pellet weight for pellet pressing:

A. take dia &amp; approx. height desired

1. calculate volume in cc. (i.e.  $\frac{(1.22\text{cm})^2 \cdot 0.35\text{cm} \cdot \pi}{4} = 0.41\text{cc}$ )

B. Assume some reasonable 'green' density (within pressed pellet)

0.6-0.8 (60-80%) usual. for metals &gt; 0.70 w/ small

ex. part. dia. (i.e. 3mm).

C. density theoretical  
$$\frac{0.41\text{cc}}{0.8} \times 9.0 \frac{\text{g}}{\text{cc}} \approx 3\text{g of part.}$$

I pressed @ between 16,000 &amp; 20,000 psi.

low side for pure metal  $\therefore$ 
$$\frac{X}{(dia)^2} = \text{desired pressure} \quad \text{where } X = 1^{\text{st}} \text{ side pressure}$$
$$X \approx 4,000 \text{ for } 0.48'' \text{ dia. die.}$$

4/24/89

#1 - Cu wt% Cu 28.7

wt% holes 36.0

Hole Concentration Conversion Formula:

Data: wt% Cu (total): 28.7  
wt% holes: 36.0see  
page after  
next

$$\frac{\text{wt\% holes} - \text{wt\% Cu}_{\text{tot}}}{\text{Cu}_{\text{tot}}} = \frac{36 - 28.7}{28.7} = 0.254$$

average over  
valence

∴ add Cu valence (2) = 2.25 = average valence Cu

$$2.25 (\text{Cu}_{\text{tot}}) = 2.25 (3) = 6.75 \text{ total Cu val}$$

↑  
from sample  
2.25

$$y \text{ Ba}_2 \text{ Cu}_3$$

$$+ 7.00 \text{ total Ba+Y val}$$

$$\frac{13.75}{4}$$

2.2 3  
4

total charges

Take total charges / divide by two for  $O^{2-}$ 

$$13.75 / 2 = 6.88 \text{ O atoms} \Rightarrow y \text{ Ba}_2 \text{ Cu}_3 \text{ O}_{6.88}$$

2.25

## Notes to Kristy concerning PELLE FORMING precalculations

To estimate pellet weight for pellet pressing:

A. take dia & apprx. height desired

1. calculate volume in cc.  $(1.2 \frac{(1.22\text{cm})^2}{4} \times 0.35\text{cm} \times \pi) = 0.41\text{cc}$

B. Assume some reasonable 'green' density (unfired pressed pellet)

0.6-0.8 (60-80%) usual for metals > 0.70 w/ small

ave. part. diam. (ie. 3mm).

$(0.41\text{cc} / 0.8) \times 9.0 \frac{\text{g}}{\text{cc}} \approx 3\text{g of part.}$  ← density theoretical

I pressed @ between 16,000 & 20,000 psi.

low side for pure metal  $\therefore$

$\frac{X}{(\text{dia})^2} = \text{desired pressure}$  where  $X = 1^{\text{st}} \text{ side pressure}$

$X \approx 4,000 \text{ for } 0.48'' \text{ dia. die.}$

DATE: 3/1/89  
 PARTICLE ANALYZER:

 SOLVENT: 150  
 SAMPLE: 150

## • CONDITIONS

 SOLV. VISC: 2.10 (CP)  
 SOLV. DENS: 0.79 (G/CC)  
 SAMP. DENS: 2.61 (G/CC)  
 D(CRUS): 10.0 (PH)  
 D(CHE): 0.10 (PH)  
 D(CDI): 1.00 (PH)  
 SPEED: 500 (RPM)

TIME: 0 H 13 MIN 47 SEC

DATE: 3/1/89

TIME: 0 H 13 MIN 47 SEC

ABSORBANCE

0.0 0.5 1.0

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 DATE: 3/1/89  
 PARTICLE ANALYZER:

 SOLVENT: 150  
 SAMPLE: 150

## • CONDITIONS

 SOLV. VISC: 2.10 (CP)  
 SOLV. DENS: 0.79 (G/CC)  
 SAMP. DENS: 2.61 (G/CC)  
 D(CRUS): 10.0 (PH)  
 D(CHE): 0.10 (PH)  
 D(CDI): 1.00 (PH)  
 SPEED: 500 (RPM)

TIME: 0 H 7 MIN 36 SEC

DATE: 3/1/89

TIME: 0 H 7 MIN 36 SEC

ABSORBANCE

0.0 0.5 1.0

0.0 0.5 1.0

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# Analytical Results for C3 HV/LD STUDY - H6es

IBM

IBM  
RESEARCH CENTER

ANALYTICAL  
LABORATORY

Request for Analysis

Use Ball Point Pen

REQUESTOR <u>T. S. Hien</u>	PROJECT NO.	REQUEST NO.
DEPARTMENT	LOCATION	ROOM <u>25-225</u> PHONE
REQUESTOR'S SAMPLE IDENTIFICATION <u>H6es, LDex</u>		
APPROXIMATE COMPOSITION AND HISTORY OF SAMPLE <u>Y<sub>2</sub>O<sub>3</sub> Co Oxide</u>		
ANALYSES REQUESTED		
ANALYSIS METHOD		
ANALYTICAL RESULTS		
	H.D.	L.D.
Wt% <u>H6es</u>	33.5	34.2
<del>Wt% Co</del>	(27.5)	(27.2)
(	2.31	2.26
	6.81	7.16g
$\frac{\text{H.D.} - \text{L.D.}}{\text{H.D.}} \times 100 = \%$		
Aster. Recor: <u>LDex</u> 28.7 <u>Wt% Co</u> ← <u>2.86</u> <u>pure Co spec</u> 36 <u>h6es</u>		
DATE SUBMITTED <u>3/20/87</u>	DATE REPORTED <u>3/24/87</u>	NOTES/WORK REFERENCE <u>1/11/84 p. 12</u>
ANALYST <u>T. S. Hien</u>	APPROVAL	

No

Recalculating Pre HD, LD values w/ 28.7% C<sub>w</sub>

$$\text{HD holes } 33.5 \therefore \frac{33.5 - 28.7}{28.7} = 0.167$$

$$2 + 0.167 = 2.167 (3) = +6.50$$

$$\begin{array}{r} + 7 \\ 13.50 \end{array} / 2 = 6.75 \Rightarrow \text{Y Ba}_2\text{Cu}_3 \text{ } ^{2.167} \text{ } ^{0.675}$$

$$\text{LD } \frac{34.2 - 28.7}{28.7} = 0.192 \quad 2.192 (3) = 6.58$$

$$\begin{array}{r} + 7 \\ 13.58 \end{array} / 2 = 6.79$$

$$\therefore \text{Y Ba}_2\text{Cu}_3 \text{ } ^{2.192} \text{ } ^{0.679}$$

with original anal. C<sub>w</sub> values

$$\text{HD } \frac{33.5 - 27.5}{27.5} = 0.22 \quad 2.22 (3) = 6.66 + 7 = 13.66 / 2 = 6.83$$

$$\text{LD } \frac{34.2 - 27.0}{27} = 0.27 \quad 2.27 (3) = 6.81 + 7 = 13.81 / 2 = 6.90 (5)$$

$$\text{w/ ave. } 27.5 + 27 = 27.25$$

$$\text{LD } \frac{34.2 - 27.25}{27.25} = 0.25 (5) \quad 2.255 (3) = 6.765 = 13.765 / 2 = 6.88$$

$$\text{HD } \frac{33.5 - 27.25}{27.25} = 0.23 \quad 2.23 (3) = 6.69 \text{ } ^{0.6845} \text{ } ^{6.88}$$

Composition #	Rel Pellet density (%) *	Actual Density	Green Rel δ	Green act δ
1	84 (90.8)	5.34	<del>62.8</del> 4.0	
2	<del>98.8</del>	5.95	61.5	3.90
3	71	4.52	60-	3.82
4	77.8	4.95	62	3.93
5	87 (91)	5.54	<del>63.4</del> 4.03	

\* after 1h sinter @ 950C